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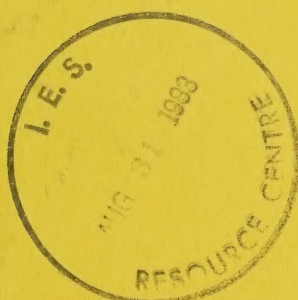
COMPENDIUM OF ENVIRONMENTAL GUIDELINES AND STANDARDS FOR
INDUSTRIAL DISCHARGES, 1983.

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**COMPENDIUM OF ENVIRON-
MENTAL GUIDELINES AND
STANDARDS FOR INDUSTRIAL
DISCHARGES**



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COMPENDIUM OF ENVIRONMENTAL GUIDELINES AND STANDARDS FOR INDUSTRIAL DISCHARGES

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PREFACE

This compendium has been prepared with the aim of assisting countries interested in introducing industrial discharge standards as part of their environmental pollution abatement strategy. To describe ways in which countries have already started to deal with the problem, examples of existing abatement strategies and standards have been collected from a number of countries. The selection of the countries was made to illustrate a number of different approaches that might be taken. Similarly, for the selection of the industries to be included in the compendium, the advice was sought from a number of experts on which might be of most interest.

The information presented concerns mainly national standards and guidelines, since extending the text to include the regulations from subsidiary administrative levels would have unduly increased the size and complexity of the compendium. However, it should be noted that in some countries these levels have considerable powers in the field of pollution control and often have the power to impose more stringent requirements than those established on the national level.

The initial work on the compendium was carried out by Mr C.J. Jackson who reviewed the available reference material and subsequently prepared the first draft of the document. This draft was reviewed by experts in the countries mentioned in the compendium who provided comments and, in many cases, additional reference material for inclusion in the document. Mrs J. Petersen and Dr H.W. de Koning prepared the final manuscript on the basis of the comments and additional information received and also edited the final version. Finally, the efforts of Miss M. Fitzsimmons in preparing the manuscript for publication are gratefully acknowledged. It should be emphasized that the views expressed should not be construed as representing the decision or the stated policy of the World Health Organization.

1. SUMMARY

The compendium consists of two parts. After an introductory chapter describing the various approaches to pollution control and regulation of industrial discharge, profiles are presented for 13 industries, each containing an outline of the processes involved, an indication of the sources of pollution, and appropriate treatment methods. Some information is also given on monitoring, enforcement and penalties for non-compliance. Each industry profile has a list of references for readers wishing to pursue the subject at greater depth. The industries surveyed are:

Brewing and distilling - Wastewaters from breweries and distilleries have a high suspended solids content and a high BOD. Guidelines for the discharge of such wastes are presented from the Federal Republic of Germany (FRG), India and the United Kingdom (UK).

Cane sugar - Cane sugar wastewaters together with wastewaters from floor and equipment washing constitute the major sources of pollution in this industry. BOD, pH and total suspended solids are all of concern as pollutants. The US Environmental Protection Agency (EPA) has developed effluent guidelines and standards for a number of different regions of the country. Those for the State of Louisiana have been given as an example of those specified in the USA for raw cane sugar.

Cement - Discharge standards applicable to the cement industry from Canada, France, FRG, Japan, Sweden, the UK and the USA are presented in the text. In general the concern of the regulatory authorities has been to control particulate emissions in the exhaust gas stream; however the USA also controls the pH and suspended solids in waste water from the industry.

Chlor-alkali - Chlorine and caustic alkali are usually produced in either diaphragm or mercury cells. Both types may give rise to discharges of chlorine to the atmosphere while mercury cells may produce mercury containing discharges. Standards for the discharge of mercury are presented from Canada, FRG, Japan, Sweden and the USA. The quoted USA limitations cover both processes and include chlorine, total suspended solids, copper, lead, nickel and pH as well as mercury.

Fertilizers - Depending on the particular fertilizer being produced, the emission of fluorides, ammonia, nitric acid, ammonium nitrate, urea dust, nitrogen acids and dust may be of concern. Effluent limitations relating to the manufacture of fertilizers are presented from India, Japan, the UK and the USA.

Hydrochloric, nitric and sulfuric acids - For this industry, hydrogen chloride from the manufacture of hydrochloric acid, nitrogen oxides from the manufacture of nitric acid and sulfur dioxide from the manufacture of sulfuric acid constitute the main pollutants. Emission standards are given from Australia, France, FRG, Japan, Sweden, the UK and the USA.

Industrial organic chemicals - Wastewaters from organic chemical plants may be contaminated with raw materials used, intermediate products, finished products and/or possibly toxic by-products. Other contaminants of concern include oils, suspended solids and catalysts. Effluent limits applicable to this industry have been quoted from India and the USA.

Iron and steel - Pollution may arise at each stage of the iron and steelmaking process. Suspended particulate matter emissions are of special concern, while for the ironmaking and steelmaking processes the problem of solids and cyanides in the exhaust gas and washing water is also of importance. Effluent guidelines and limitations pertaining to the industry from Canada, France, FRG, Japan, Sweden, the UK and the USA are given.

Metal finishing - The wide range of metal finishing processes used gives rise to an equally wide range of pollutants. High concentrations of various metals (iron, copper, zinc, nickel, chromium and lead) various acid wastes (nitric acid, phosphoric acid and acetic acid), electrolytes (sodium nitrate and sodium chloride) and sludges, slurries and metallic oxides or hydroxides. Discharge standards are presented from Canada, FRG, India, Italy, Singapore, the UK and the USA.

Petrochemicals - Dissolved and suspended hydrocarbon effluents may arise from both the basic steam cracking and the various secondary petrochemical processes. In addition, organochlorine compounds, chlorinated hydrocarbons and toxic nitrates may be of concern in certain cases. The US emission standards for vinyl chloride from a number of specified manufacturing processes, as well as US effluent limitations for waste waters from petrochemical plants are given.

Petroleum refining - As with the petrochemicals sector, the emission of hydrocarbons is of major concern. However, emission of spent amine solution, desalter water, sulfidic spent caustic, washings containing phosphoric acid, carbon monoxide etc., are also of concern from particular processes. Discharge limits from Canada, France, FRG and the USA are presented.

Pulp and paper - Suspended and dissolved solids, oxygen consuming substances and coloured lignin compounds are all pollutants of concern in this industry. Reduced sulfur compounds and sulfur dioxide may also be produced in certain treatments. Effluent guidelines from Australia (Tasmania), Canada, France, FRG, Japan, Sweden, the UK and the USA are given.

Tanning - In the hide preparation process, the main concern is with wastewaters heavily contaminated with organic matter. Effluents from the tanning process may include organics, suspended solids, oxygen-consuming compounds, chromium (III and VI), sulfates, sulfides, chlorides, ammonia and coliforms. Frequently tanhouse effluents may be discharged into public sewers for treatment with domestic sewage and appropriate effluent limitations may be specified. While no legally enforceable standards have been laid down for tannery discharges in France, FRG and the UK, relevant recommendations relating to such effluents have been given. Discharge limits for tannery effluents are given from India, Italy, Singapore and the USA. These limits are legally enforceable in the country concerned.

2. APPROACHES TO THE REGULATION OF INDUSTRIAL DISCHARGES

The effect of the discharge of waste products into the environment has long been a subject of concern in the industrialized countries of the world. Of particular concern has been the discharge of industrial wastes. As industrialization has spread to the developing countries, the subject is now becoming of increasing importance to them.

2.1. General quality standards

Although approaches to the problem vary from country to country, it is fair to say that all start from a desire to achieve and/or maintain acceptable standards of air and water quality. Some countries take the step of technically specifying these standards, even though many difficulties are inherent in establishing such specifications.

The problem of deciding on acceptable concentrations of the various pollutants is complicated because of inadequate knowledge of the pollutants' effects, particularly in small sustained concentrations, on human health and on animal and plant life. These effects must be weighed with other, often conflicting, economic and social aspects. Thus, in some cases, it has been found desirable to establish special standards for certain areas such as nature reserves or areas of special natural or cultural interest. Water quality standards in particular often vary according to the use to which the water is to be put (e.g. stricter standards may be established for streams used as drinking water sources).

Practical problems may arise in applying general air and water quality standards to individual sources of pollution. Complex modelling may be required to determine the discharge standard such that the overall concentration of a given pollutant satisfies the general standard.

Notwithstanding these problems, general quality standards have been the subject of both national and international attention. At the national level most industrialized countries have established standards or norms to provide safeguards against the harmful effects of the more common and widespread pollutants. Further emphasis is now being placed on the more toxic pollutants and those whose effect might only be observed after many years of exposure.

On the international level WHO has for many years been involved in health effects research through collaboration with national institutes. An integrated programme on the assessment of health effects of environmental conditions was instituted in 1973 with financial support from the United Nations Environment Programme under the title WHO Environmental Health Criteria Programme. The list of chemicals and physical hazards dealt with under this programme is regularly reviewed. To date about 20 WHO Environmental Health Criteria documents have been issued and many more are in preparation. The International Agency for Research on Cancer (IARC) is conducting a separate programme for the evaluation of potentially carcinogenic chemicals in the environment the results of which are published in a series of IARC Monographs on the Carcinogenic Risk of Chemicals to Humans of which about 23 volumes have appeared to date.

It can be expected that general air and water quality standards will continue to provide a basis for the evaluation of the effectiveness of emission controls. They will also continue to assist in the setting of priorities and targets to be achieved by such controls as they automatically bring the concept of the receiving capacity of the environment into consideration. For example, Japan has prescribed stricter dust emission standards for the manufacture of iron and steel in highly industrialized areas.

2.2. Discharge standards

Discharge standards have been introduced in a number of countries, sometimes in isolation and sometimes in conjunction with general quality standards or other control mechanisms. The character of the standards has of course, been strongly influenced by the historical, administrative and legal traditions of the country involved.

2.2.1. Scope

In its simplest form, a discharge standard covers all industries throughout the entire country. This approach has been adopted, for example, in Italy and Singapore. In Italy current legislation specifies maximum permissible concentrations at ground level for industrial air pollutants. However in both countries, it has been found necessary to establish separate sets of standards for different types of receptors. Thus in Italy the 1976 law prescribing rules for the protection of water against pollution distinguishes between discharges into surface waters and those into public sewers.

In Hungary, industrial and combustion operations have to report annually on their air-contaminating activity. If this activity exceeds the acceptable levels, they have to pay fines. The level of the acceptable emission is determined according to the following features: the base-load of the given area, the height of the emission point, the type of contaminants, other sources of emission in the vicinity and the category of the protection of the area (highly protected, protected or an industrial area).

For control of the quantity of contaminants discharged into sewers, a concentration-based regulation is used in Hungary. The country is divided into six water-quality protection categories in which different tolerance levels are valid. However, tolerance levels are expressed as concentrations, and the total quantity of discharged material is not limited. The decree in force at present (number 28/1978.MT) gives limits for thirty chemicals, one bacteriological (referring to disinfected sewage) and one toxicological parameter. For example, the following values are permitted for the concentration of organic substances (measured by COD), 50 mg/l in the most protected watershed areas and 150 mg/l in

the least protected watershed areas. The strictest limit is for mercury: 0.002 mg/l and 0.02 mg/l respectively, the least severe one is for the amount of total salt concentration: 1000 mg/l and 2000 mg/l respectively.

In the State of Rio de Janeiro, Brazil, standards for the discharge of effluent have been drawn up in FEEMA DOC.NT.202 with a view to the speedy development of waste treatment systems for polluting industries. These standards include the federal norms, which lay down minimum discharge requirements and are intended to take into account the nature of the various pollutants found in wastewater. General guidelines have also been developed to establish maximum permissible concentrations for toxic pollutants with reference to the most noxious pollutants and those which are not degraded in the environment.

The major difference between the approach to pollution control adopted in the State of Rio de Janeiro and that followed in the many other countries lies in the use made, to a limited extent, of the assimilative capacity of the environment. Such an approach calls for a reasonable amount of knowledge of the bodies of water, i.e. basically data on water quality (from monitoring), and requires the development of mathematical models to simulate the impact of future discharges and the proposed control measures.

Standards for specific industries, especially those producing particularly noxious effluents, have also been introduced. This was the approach adopted by the US Environmental Protection Agency in laying down effluent limitations for wastewaters from 56 "point source categories".

The final, and most specific, means of establishing discharge standards, is on a case-by-case basis. Such an approach has been adopted for the control of water pollution in the United Kingdom where effluent standards for individual plants are fixed by the local Regional Water Authority. Ten such Authorities were set up in England and Wales by the Water Act of 1973. Standards set for individual plants are not made public, although a general guide has been given by the Yorkshire Regional Water Authority. They have published "working standards" for discharges into both watercourses and public sewers. The situation will change when Part (2) of the Control of Pollution Act 1974 comes into force as standards will then be open to public scrutiny.

A distinction is often made, both in standards applicable to all industries and ones specific to particular industries, between new and existing plants. Where this distinction is made, existing plants are usually initially granted a more lenient standard and then allowed a period of grace before being required to comply with the ultimate standard. New plants are usually required to comply with the ultimate standard from the start.

It is possible, in some cases of water pollution, to permit the discharge of industrial wastes into public sewers on the payment of an appropriate fee. This system is used in France, the FRG, the UK and the USA. Charges imposed are related both to the quality and characteristics of the effluent. The public authority receiving the waste discharge is thus recompensed for the effort involved in disposing of it and, at the same time, the scale of charges ensures that the plant has an economic incentive to improve the quality of the effluent. It must be remembered when considering such a course that some pollutants, such as mercury, are so objectionable that they should not be allowed to enter watercourses at all.

2.2.2. Legal status

The manner in which discharge standards are promulgated varies widely. Certain standards may be incorporated in legislation, while others may be made under enabling legislation. The effectiveness of such legislation will, of course, depend on the extent to which it is enforced in practice and the prescribed penalties actually imposed. Another point that bears on the effectiveness of enforcement is the question of who is entitled to bring a prosecution. In the case of the United Kingdom, when Part (2) of the Control of Pollution Act 1974 comes into force, it will be possible for members of the public as well as the Regional Water Authorities to take legal action against non-compliers.

Non-mandatory guidelines may also be used in certain cases. These may be published either by a governmental authority, such as the Swedish National Environment Protection Board or by a non-governmental body, such as the Länderarbeitsgemeinschaft Wasser in the Federal Republic of Germany. It is usual in the preparation of these guidelines to consult all the interested parties. As the guidelines are non-mandatory the co-operation of industry is especially important.

An interesting situation has developed in India where the Indian Standards Institution has published discharge standards for a number of industries. While these are necessarily only suggested levels, they have in some cases been adopted and made enforceable by a number of State Boards responsible, under the Water (Prevention and Control of Pollution) Act 1974.

2.2.3. The "Best Practicable" approach

A different approach to industrial air pollution has been developed in the United Kingdom. Atmospheric pollution caused by effluents from chemical and manufacturing plants is governed by the Alkali etc. Works Regulation Act (Alkali Act) originally dating from 1863. The Alkali Act was the result of the public outcry which followed the establishment in the UK of the Le Blanc process for the manufacture of sodium carbonate. This process produced as a by-product, and vented, large quantities of hydrogen chloride. A Royal Commission was appointed which made the finding that if 95% of the hydrogen chloride was trapped, the remainder could be vented without serious risk. The Act has been repeatedly amended, extended and consolidated. The last consolidation, of 1906, lays down statutory emission limits only for hydrogen chloride and sulfur trioxide. However, it also contains a List of Scheduled Works, and lays down the same basic principle established by the original Act, i.e. that "the best practicable means" must be used to prevent the emission of noxious or offensive substances into the atmosphere and for rendering harmless any that are so emitted. This principle has been taken over by the Health and Safety at Work Act of 1974 which has partially replaced the Alkali Act.

No definition of "best practicable means" is given in either Act. However, the governmental body responsible for the control of air pollution (the Alkali and Clean Air Inspectorate) has published information on a number of industries as a guide to the means by which it would determine whether "best practicable means" are being used. Such information often includes guidance on discharges in the form of "presumptive limits". These are the emission limits that would normally be accepted by the Inspectorate as evidence that the "best practicable means" are being used. They can, however, be varied for certain plants, after consultation with the plant management, if this is considered desirable. Such a move might be made in an area of high background pollution.

Control is exercised by the Inspectorate both by inspections prior to start-up, and by routine inspections of operating plants. Such routine inspections include measurements of pollutant emission levels. When the Inspectorate finds that requirements are not being met it is able to take legal action. However, prosecutions are fairly rare as a warning to management is usually sufficient to remedy the situation.

While this case-by-case approach has been criticized on the grounds that air pollution is no longer a purely local problem, and also because it would seem to discriminate against plants located in the polluted industrial areas, the proponents stress the inherent flexibility and the way in which technical feasibility can be weighed against economic and social factors.

The Swedish approach requires prevention measures based on the most effective technical devices and methods existing in a region, with due regard having to be paid to the effects of the nuisance and the usefulness and economics of the activity. The approach was adopted in 1969 with the passing of new legislation for the protection of the environment and the formation of the National Environment Protection Board from the former National Committee for Air Conservation.

The United States has also pursued the objective of ensuring that the best technology available is used in pollution abatement. A comprehensive programme was established in 1972 under the Federal Water Pollution Control Act Amendments to "restore and maintain the chemical physical and biological integrity of the nation's waters". A deadline of 1 July 1977 was set for existing industrial direct dischargers to achieve effluent limitations requiring the "best practicable control technology currently available" (BPT). Also, these dischargers were set another deadline of 1 July 1983 to achieve effluent limitations requiring the application of the "best available technology economically achievable" (BAT). New sources were to be required to comply with the new source performance standards (NSPS) based on "best available demonstrated technology". Limitations were also to be set for new and existing dischargers to publicly-owned treatment works.

The US Environmental Protection Agency (EPA) was unable to promulgate many of the deadlines contained in the Act and was consequently sued by several environmental groups. A "settlement agreement" was reached which required the EPA to develop a programme and meet a schedule for controlling 65 "priority" pollutants. Several of the basic elements of the settlement agreement programme were incorporated into the Clean Water Act of 1977.

Under this Act the emphasis has shifted to the control of "toxic" pollutants. These include the 65 "priority" pollutants in the settlement agreement as well as other classes of pollutants declared toxic under the Act. A new deadline of 1 July 1984 has been set for the achievement of BAT effluent limitations for toxic pollutants. For "conventional" pollutants (BOD, total suspended solids, fecal coliform, pH and oil and grease) the 1977 Act requires effluent limitations requiring the application of the "best conventional pollutant control technology" (BCT) to be achieved by 1 July 1981. For non-toxic, non-conventional pollutants, the Act requires the achievement of BAT limitations within three years of their establishment or by 1 July 1984, whichever is the later, but not later than 1 July 1987.

In the field of air pollution prevention and control the Clean Air Act Amendments of 1970 authorized the commencement of a national programme. The programme was reinforced by further amendments to the Clean Air Act in 1977. The Clean Air Act standards of performance reflect the degree of emission control achievable by application of the best system of continuous emission reduction that has been adequately demonstrated, taking into consideration cost, health and environmental impacts not related to air quality, and energy requirements. This technology is commonly referred to as "best demonstrated technology" (BDT). The emission standards selected are based on a reference test procedure that must be used to show compliance with the regulation.

Air pollution from new sources has been controlled by the issuing of New Source Performance Standards (NSPS). Also, the EPA has been required to issue National Emission Standards for Hazardous Air Pollutants (NESHAPS) at a level judged to provide an ample margin of safety to protect the public health. The regulation may take the form of an emission standard or a design, equipment, work practice, or operational standard if an emission standard is not feasible. NESHAPS apply both to new and existing sources and regulations have been developed for asbestos, beryllium, mercury and vinyl chloride. Benzene and arsenic have been listed and regulation is under development.

The EPA limitations for both air and water pollution are always based on a thorough study of the industry concerned. Raw materials, products and processes are studied, residual characteristics identified and constituents of the discharges to be subject to limitation chosen. Control and treatment technologies are identified and information (both economic and technical) is gathered on their application.

2.2.4. Monitoring

Procedures for ensuring compliance with discharge standards will clearly be ineffective in the absence of arrangements for monitoring the pollutant content of effluents.

Monitoring in the United Kingdom has already been mentioned in connexion with the control of atmospheric discharges by the Alkali and Clean Air Inspectorate. Provision for monitoring is also made in other countries. Canada, for example, requires monitoring of atmospheric emissions of mercury and of liquid mercury-containing effluents from chlor-alkali production. The 1977 Chlor-Alkali Mercury Liquid Effluent Regulations require the owner of a plant to install sampling equipment, to take a composite sample of effluent every day and to analyse it, to measure and record the effluent flow rate every day, and to calculate the actual amount of mercury discharged.

2.2.5 Expression of discharge standards

Effluent discharge standards may be expressed:

- (i) in terms of the concentration of the pollutant in the effluent stream;
- (ii) in terms of the allowable quantity of pollutant discharged per unit of raw material input or product output.

The first of these measures, that of concentration, is theoretically determinable at a single instant but in practice is usually taken as the average concentration of a number of samples. On the other hand the quantity measure, being flow dependant, must be determined by a series of analyses of concentrations and flow rates over a specified time period. Such standards are thus not suitable for industries such as tanning where batch processes are used.

On the regulation of the discharge of wastes, Hungary has enacted general regulations defining the quality of wastes as dangerous or non-dangerous. The separation of non-dangerous wastes and the classification of the other category into dangerous classes was not made according to industrial branches. Neither are the tolerance levels of discharge of wastes defined in terms of production units.

The control of wastes and the activity of rendering wastes harmless are regulated by decree number 56/1981/XI.18./MT of the Council of Ministers which entered into force on 1.1.1982. The detailed rules of this decree are defined by the Ministers concerned or by the institutions of national authority in agreement with the president of the National Office for Environmental Protection and with the Minister of Health.

According to paragraph 20 of decree number 56/1981/XI.18./MT "dangerous waste is all remaining material after the production or after any other activity, the whole or the decomposition product which may act as a harmful toxicant or infectant, in direct or indirect way, suddenly or delayed, to human life, to health and/or to any living substance and which cannot be used further or marketed by the producer".

In Kenya, industry by industry discharge standards do not exist. Instead there are generalized water pollution control standards which vary with the type of industry, the location, volume of receiving waters, or whether the effluent is discharged into a water course or a municipal sewer. There also exist rules and regulations which are used as guidelines for factory establishment and extension covering wastewater treatment.

2.3. Product and process standards

In some instances pollution control has been achieved by the use of product or process standards. Thus, in some areas the problem of discharge of lead from the burning of petrol has been confronted by prohibiting the addition of lead to petrol. Similarly the problem of sulfur emission from the burning of fuel-oil has sometimes been confronted by specifying maximum concentrations of sulfur in the fuel oil. The problem of aquatic blooms caused by phosphatic detergents has also been addressed by the removal of phosphates from detergents.

An example of a process control is the prevention of mercury emissions from chlor-alkali manufacture in Japan by the mandatory replacement of mercury cells by diaphragm cells.

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3. INDUSTRY PROFILES

3.1. BREWING AND DISTILLING

Brewing is the production of a fermented beverage of low alcohol content from various types of grain. A product of higher alcohol content can be obtained by the distillation of alcohol-containing liquors produced by means of various fermentation processes.

3.1.1. Outline of process

The grain most commonly used for brewing is barley. This contains starch, which has first to be converted into sugar before fermentation can take place. Conversion is achieved by means of the process known as malting, in which the grain is steeped in water and then spread out in thin layers to germinate. During germination, the enzyme diastase is formed, which converts the starch into maltose. Growth is then stopped by heating the sprouted grain in a kiln.

Malting is followed by mashing, in which the malt, after grinding, is extracted with hot water in a mash tub to give a liquid called wort. To manufacture beer, the wort is then boiled with hops in a brew kettle so as to give a beer of the desired flavour.

After separation of the spent hops, and cooling to the correct temperature, the wort is passed to a fermenter and yeast added to induce fermentation. The yeast enzymes convert the sugar present in the wort into alcohol and carbon dioxide. The beer leaving the fermenter may then be stored to allow further fermentation to take place. Filtration, carbonation etc., can also be carried out to make a beer of the type desired. The type of liquor produced from distillation will depend on the alcoholic liquid used as a base. Thus the base for brandy is wine, while whisky is distilled from a fermented wort derived from barley. Rum is distilled from a product obtained by the fermentation of molasses. Distillation may be carried out in a simple batch-type pot still or in a continuously operating fractionating column. The alcohol content can vary from about 60% to nearly 100%.

3.1.2. Sources of pollution

Malting gives rise both to liquid wastes derived from the steeping of the barley and to solid wastes consisting of the sprouts and rootlets screened out during the preparation of the malt. The steep water, with a volume of up to 9 times that of the barley, contains foreign matter and soluble material extracted from the grain. Liquid wastes from malt-houses can be treated in conventional biological filters.

Wastes from fermentation and subsequent operations include spent grain, hops and yeast, liquors from spent grain, yeast washing and pressing of yeast wastes, and wash waters from the washing of equipment, casks, bottles, barrels, etc. The liquid wastes have a high suspended solids content and a high BOD. They are usually discharged into public sewers, sometimes after biological pretreatment.

In distillation, the alcohol removed is only a small fraction of the original base liquid and consequently considerable amounts of effluent remain for disposal. In whisky manufacture, for example, this pot ale or spent is fed to multiple-effect evaporators, where 96% of the water is removed. After further treatment, a product known as distillers' dried solubles is produced. Some malt distillery effluents are, however, treated biologically, disposed of to land, or discharged into the sea or into public sewers.

3.1.3. Discharge standards

Germany (Federal Republic)

Guidelines for wastewaters from breweries and malt-houses, after treatment, have been published by the Länderarbeitsgemeinschaft Wasser, and are shown in Table 1A. It is stated that such wastewaters should be treated only when it is not possible for them to be disposed of together with domestic wastes.

Table 1A: Guidelines for discharges from breweries and malt-houses (FRG)

Item	Recommended values after:		
	Mechanical treatment	Complete biological treatment	Partial biological treatment
Settleable solids (ml/litre)	0.3	0.3	0.3
Suspended solids	Not to be visible to the naked eye	-	-
Undissolved substances (ml/litre)	-	20	20
Putrescibility	-	Negative	-
Potassium permanganate consumption (mg/litre)	-	80	150
BOD (mg/litre)	-	25	80

India

The tolerance limits for distillery effluents discharged into surface waters are specified in Indian Standard IS: 2490, part II, (1974), while general tolerance limits for industrial effluents discharged into public sewers are contained in Indian Standards (IS: 3306-1974). These standards are shown in Table 1B. IS: 3306-1974 specifically states that beer or distillery slops containing solids must not be discharged into public sewers.

The limit of 600 mg/litre for suspended solids contained in effluent discharged into public sewers may be increased to 750 mg/litre by the local authority. The requirement for BOD₅ in discharges to public sewers may be increased or decreased by the local authority. Similarly the BOD₅ limit for discharges to inland surface waters may be increased to 100 mg/litre on a temporary basis where existing distilleries have difficulty in complying with the 30 mg/litre limit.

Table 1B: Tolerance limits for effluent discharges (India)

Item	Tolerance limits for:	
	Distillery effluents into inland surface waters	Brewery and distillery effluents into public sewers
Suspended solids (mg/litre)	100	600
pH	5.5 - 9.0	5.5 - 9.0
BOD ₅ (mg/litre)	30	500
Colour and odour	Must be absent	-

United Kingdom

Each discharge of brewery or distillery effluents, either to surface waters or to public sewers, is considered on its merits by the appropriate Regional Water Authority. No discharge is permitted without the consent of the competent Authority. Any such consent to discharge effluent into a watercourse may be made subject to the fulfillment of certain conditions; contraventions of these conditions are punishable by fines. A consent to discharge effluent into a public sewer may also be made subject to certain conditions with the Authority retaining the additional right to require the discharger to pay certain charges for the treatment of the effluent.

The Yorkshire Water Authority has given some guidance on the discharge into streams of effluents arising from the processing of natural organic compounds. These must be similar in character to domestic sewage and respond to biological treatment in a similar way. The relevant consent working standards for such effluents (which include brewery waste) are shown in Table 1C.

Table 1C: Consent working standards for brewery wastes (Yorkshire Water Authority, UK)

Characteristic	Limiting value
Suspended solids (mg/litre)	30
BOD (mg/litre)	20
4-hour permanganate value (mg/litre)	25
pH	6 - 9

For discharges into public sewers, the Yorkshire Authority specifies that the pH of all trade effluents must be in the range 5 - 10. It has the right to control the concentration of other constituents, including suspended solids and live yeast. For suspended solids a possible limit of 500 mg/litre is given, but the actual limits are subject to negotiation between the Authority and the discharger.

3.1.4. References

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2. Indian Standards Institution, Tolerance limits for industrial effluents discharged into inland surface waters: Distillery industry, New Delhi, IS: 2490, part II (1974).
3. Indian Standards Institution, Tolerance limits for industrial effluents discharged into public sewers, New Delhi, IS: 3306, first revision (1974).
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3.2. CANE SUGAR

In the cane sugar industry, the juice extracted from the cane is first purified and then concentrated and refined to give liquid sugar or further concentrated to crystalline sugar.

3.2.1. Outline of process

After manual or mechanical harvesting, the cane is washed to remove extraneous material, cut up into short lengths and crushed between rollers to extract the juice. This is screened and then treated with lime to prevent inversion of the sucrose. It is then heated, clarified to remove insoluble compounds, and concentrated in multiple-effect evaporators to give a syrup with a water content of 30-40%. This syrup is further concentrated in vacuum pans,

when a mixture of sugar crystals (raw sugar) and syrup (molasses) is formed. From this mixture the sugar is separated by centrifugation. The raw sugar is refined in order to obtain various market products.

3.2.2. Sources of pollution

Cane washing can be a major source of pollution, especially where the cane is harvested mechanically. It is not possible in this case to exclude dirt and impurities to the extent feasible with manual harvesting. In addition, mechanical harvesting causes greater damage to the cane, and therefore increased contamination of the wash water with sugar. However, the trend seems to be towards increasing use of mechanical harvesting because of rising labour costs. In addition to substantial concentrations of sugar, cane wash water also contains high concentrations of suspended solids. These may be colloidal in character and difficult to remove by conventional coagulation procedures.

Other wastewaters that cause pollution problems include those from floor washing and from washing of equipment, particularly during weekend shutdowns. The carryover of sugar into evaporator condensate, as a consequence of foaming can result in condenser water also constituting a major source of pollution. Removal of scale from heating surfaces with caustic soda and then with inhibited dilute hydrochloric acid gives rise to alkaline and acid wastes.

Wastewaters from raw sugar factories are usually treated by stabilization in impounding lagoons with the space available often being subdivided into three or four basins in series. As the organic acids produced inhibit the growth of microorganisms, it is necessary to neutralize these by, for example, adding lime. Oxidation ponds have also been used.

3.2.3. Discharge standards

United States of America

Under the Federal Water Pollution Control Act Amendments of 1972, the US Environmental Protection Agency has issued effluent guidelines and standards for the sugar processing point source category. These cover raw cane sugar processing in a number of different areas (Louisiana, Florida and Texas, Hawaii, and Puerto Rico), crystalline cane sugar refining and liquid cane sugar refining. In establishing these effluent guidelines, account was taken of all available information and relevant factors such as age and size of plant, raw materials, manufacturing processes, treatment technology, etc. The guidelines may be made either less or more stringent, depending on the conditions.

The effluent limitations for the State of Louisiana are given as an example of those for raw cane sugar. They represent the degree of effluent reduction attainable by the application of the "best practicable control technology currently available" (BPT), and are given separately for the continuous discharge of waste waters and for factories using waste stabilization. The limitations are shown in Table 2A.

Table 2A: Effluent limitations for raw cane sugar processing (Louisiana, USA)
(kg/1000 kg of gross cane)

Characteristic	Effluent limitations		
	Continuous discharge		Waste stabilization
	Max. for any 1 day	Max. ave. of daily values for 30 consec. days	Max. total of daily values for entire discharge period
BOD ₅ (a)	1.14	0.63	0.63
Total suspended solids (b)	1.14	0.47	0.47
pH	6.0-9.0	6.0-9.0	6.0-9.0

- (a) For barometric condenser cooling water together with treated process waste water.
- (b) For treated process waste water only.

For crystalline cane sugar refining, effluent limitations for existing refineries are given both for BPT and for the "best available technology economically achievable" (BAT). The effluent limitations for such refineries are shown in Table 2B.

Table 2B: Effluent limitations for existing crystalline cane sugar factories (USA)
(kg/1000 kg of melt)

Characteristic	Effluent limitations			
	Max. for any 1 day		Max. ave. of daily values for 30 consec. days	
	BPT	BAT	BPT	BAT
BOD ₅	1.19 ^(a) (1.02)	0.18	0.43 ^(a) (0.32)	0.09
Total suspended solids	0.27 ^(b)	0.11	0.09 ^(b)	0.035
pH	6.0-9.0 ^(b)	6.0-9.0	6.0-9.0 ^(b)	6.0-9.0

- (a) The figure in brackets applies to refineries discharging barometric condenser cooling water only.
- (b) No limitation imposed on refineries discharging barometric condenser cooling water only.

No limitations are imposed on the discharge of effluents from existing crystalline cane sugar refineries into publicly owned treatment works. The effluent limitations for new crystalline cane sugar refineries are required to meet the BAT standards shown in Table 2B.

For existing liquid cane sugar refineries, the effluent limitations are shown in Table 2C. However, no limitations are imposed on the discharge of effluents from such refineries into publicly owned treatment works.

The effluent limitations for new liquid cane sugar refineries are required to meet the BAT standards shown in Table 2C.

Table 2C: Effluent limitations for existing liquid cane sugar factories (USA)
(kg/1000 kg of melt)

Characteristic	Effluent limitations			
	Max. for any 1 day		Max. ave. of daily values for 30 consec. days	
	BPT	BAT	BPT	BAT
BOD ₅	0.78(0.45) ^(a)	0.3	0.32(0.15) ^(a)	0.15
Total suspended solids	0.50 ^(b)	0.09	0.17 ^(b)	0.03
pH	6.0-9.0 ^(b)	6.0-9.0	6.0-9.0	6.0-9.0

(a) The figure in brackets applies to refineries discharging barometric condenser cooling water only.

(b) No limitation imposed on refineries discharging barometric condenser cooling water only.

3.2.4. References

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3.3. CEMENT

Cement is a complex calcium silicate-aluminate-ferrite produced by the combination of limestone or other form of calcium carbonate with material containing alumina, silica and iron (usually clay). When mixed with water it forms a binding material for aggregates

(crushed stone, gravel or sand) in concrete. The main product (about 95% in the USA) is portland cement; for this reason, other types of cement will not be dealt with specifically here, but the pollution problems associated with their manufacture are essentially the same as those associated with that of portland cement.

3.3.1. Outline of process

The first stage in the manufacture of cement, namely the extraction of the raw materials, is not unique to the industry and will not be considered here.

After the raw materials have been extracted, they are reduced in size by crushing and grinding. The ground limestone and clay are then blended to give a feed of the correct composition for the kiln in which they are heated so as to combine to form the product known as clinker. Rotary kilns are generally used for this purpose. The kiln feed, which may be in the form either of a slurry (wet process) or of dry nodules (dry process) is introduced into the upper end of the kiln, while fuel for heating (coal, fuel oil or gas) enters and is burned at the lower end. In this way, the feed is successively heated, dried (if the wet process is being used), calcined and finally heated to incipient fusion, when chemical reaction occurs and clinker is formed. This is cooled with air, ground to a fine powder together with added gypsum (finish grinding), and passed to storage or packaging.

3.3.2. Sources of pollution

The rotary kiln is the main source of dust emissions in cement manufacture. The hot gases produced by the combustion of the fuel are pulled by forced draught up through the kiln counter-current to the raw materials flowing down it, and carry entrained dust with them from the upper end. The emissions can be reduced by certain process modifications, and by hanging a dense curtain of light-weight chain at the discharge end, but further gas cleaning is still necessary. This is achieved by means of high-efficiency electrostatic precipitators, fabric filters or venturi scrubbers, often in series with inertial collectors.

Dust emissions are also produced in crushing and grinding, blending, clinker cooling, finish grinding, and in moving finely divided material to silos and packaging equipment.

Wastewaters are produced in cement manufacture during the blending process and from the use of wet scrubbers for removing dust from the kiln exit gases.

3.3.3. Discharge standards

Canada

Cement Industry National Emission Guidelines were issued by the Department of the Environment in October 1974 for both new and existing plants and are shown in Table 3A.

Table 3A: Emission guidelines for cement plants (Canada) (lb/2000lb of clinker)

Source	Guidelines	
	New plants	Existing plants
Kiln	0.9	1.6
Clinker cooler	0.6	0.6
Finish grinding	0.1	0.1
All others	0.2	0.2

The guidelines were developed in consultation with representatives of provincial governments and industry; they are based on "best practicable technology currently available" to the industry.

France

All cement factories are subject to the provisions of the Law of 19 December 1917, as amended, on "classified establishments". In particular, Article 4 of the Law provides that no new cement factory can be brought into operation unless it has first been licensed by the Prefect. Prefects are encouraged to include in the terms of any such licence the technical requirements contained in a Circular issued in 1971 and drawn up in conjunction with the cement industry. This specifies that, under normal conditions, the dust content of the kiln exit gases must not exceed 0.150 g/Nm^3 . Under exceptional circumstances, this figure may be exceeded, but not for more than 48 hours during any one continuous period, or for more than a total of 200 hours in any one year. The same limit of 0.150 g/Nm^3 also applies to all gases other than exit gases from the kiln.

Germany (Federal Republic)

At the federal level, dust emissions from cement plants are governed by the Technical Guide for Air Quality Control of 1974, made under the Federal Law of 28 August 1974 on the prevention of pollution. The limitations are as follows:

Plants not fitted with electrostatic precipitators	75 mg/Nm^3
Plants fitted with electrostatic precipitators	120 mg/Nm^3
As above, but dust of high electrical resistance	150 mg/Nm^3

Apart from these federal requirements, North Rhineland has also introduced legislation on the licensing of cement factories. Under this licensing procedure, the maximum permitted dust emission is usually about 150 mg/Nm^3 .

Japan

The Law of 1968 on air pollution control, as amended, lays down the dust emission standards for cement plants shown in Table 3B.

Table 3B: Emission standards for dust from cement plants (Japan)

Gas flow-rate (Nm^3/h)	General standards (mg/Nm^3)	Special standards for polluted districts (mg/Nm^3)
less than 40 000	400	200
greater than 40 000	200	100

Sweden

Cement factories are subject to licensing by the National Franchise Board for Environment Protection, after consultation with the National Environment Protection Board and other authorities. The following guidelines have been issued by the National Environment Protection Board:

New kilns	150 mg/Nm ³
Existing kilns	250 mg/Nm ³

United Kingdom

Cement production works are included in the List of Scheduled Works under the Alkali Act 1906.

Information on best practicable means for cement production has been published by the Inspectorate, and certain particulate emission limits specified, as shown in Table 3C. While the limits given in Table 3C do not have the force of law, they are the maximum that will normally be accepted as confirmation that the best practicable means are being used.

Table 3C: Particulate emission limits for cement works (United Kingdom)

Source	Emission limit (mg/Nm ³)
Clinker kiln:	
New kilns	100
Other cement-handling operations	150

United States of America

Under the Clean Air Act Amendments the Federal Government was empowered to issue performance standards for new stationary sources.

The US Environmental Protection Agency has promulgated the following standards for portland cement manufacture:

Table 3D: Performance standards for new portland cement manufacture (USA)

Source	Pollutant	Emission	Monitoring requirement
Kiln	Particulate	0.15 kg/mg	No requirement
	Opacity	20%	No requirement
Clinker Cooler	Particulate	0.050 kg/mg	No requirement
	Opacity	10%	No requirement
Fugitive emission points (a)	Opacity	10%	No requirement
			Daily production rates and hours

(a) loading and unloading points raw and finished material storage

Also, under the Federal Water Pollution Control Act Amendments of 1972, the US Environmental Protection Agency has issued effluent standards and guidelines for the cement manufacturing industry. These cover the following processes:

- (i) Non leaching, where kiln dust is not contacted with water as an integral part of the process and wet scrubbers are not used to control kiln stack emissions;
- (ii) Leaching, where kiln dust is contacted with water as an integral part of the process, or water is used in wet scrubbers to control kiln stack emissions;
- (iii) material storage piles runoff, where effluents arise as a result of the runoff of rainfall from storage piles used in or derived from the manufacture of cement.

Existing plants discharging into navigable waters were required to meet the "best practicable technology currently available" (BPT) standards by 1 July 1977 and will be required to meet "best available technology economically achievable" (BAT) standards by 1 July 1984. New plants discharging into navigable waters must achieve "new source performance standards" (NSPS) while those discharging into publicly-owned treatment works must achieve "pretreatment standards for new sources" (PSNS). The BPT, BAT, NSPS, and PSNS limits are given in Tables 3E and 3F.

Table 3E: Effluent limitations for existing cement manufacturing plants (USA)

Characteristic	Max. for any 1 day		Max. ave. of daily values for 30 consec. days	
	BPT	BAT	BPT	BAT
<u>Non-Leaching</u>				
Total suspended solids (kg/1000 kg of product)	0.005	0.005	-	-
Temperature	not to exceed 3°C rise above inlet temp.			
pH	6.0-9.0	6.0-9.0	-	-
<u>Leaching</u>				
Total suspended solids (kg/1000 of product)	0.4	0.005	-	-
Temperature	not to exceed 3°C rise above inlet temp.			
pH	6.0-9.0	6.0-9.0	-	-
<u>Materials Storage</u>				
<u>Piles Runoff</u>				
Total suspended solids (mg/litre)	50	50	50	50
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

Table 3F: Maximum effluent limitations for any one day for new cement manufacturing plants (USA)

Characteristic	NSPS and PSNS
<u>Non-Leaching</u>	
Total suspended solids (kg/1000 kg of product)	0.005
Temperature	not to exceed 3°C rise over inlet temp.
pH	6.0-9.0
<u>Leaching</u>	
Total suspended solids (kg/1000 kg of dust leached)	0.4
Temperature	not to exceed 3°C rise over inlet temp.
pH	6.0-9.0
<u>Materials Storage</u>	
<u>Piles Runoff</u>	
Total suspended solids (mg/litre)	50.0
pH	6.0-9.0

3.3.4. References

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3.4. CHLOR-ALKALI PRODUCTION

Chlorine and caustic alkali are usually produced concurrently by the electrolysis of brine in chlor-alkali cells, though the same products can also be obtained by the electrolysis of fused alkali chloride in Downs cells.

3.4.1. Outline of process

In chlor-alkali cells, the chloride solution is fed into the cell and decomposed by the passage of an electric current; this can be accomplished in two different ways. In the diaphragm-cell process, contact between the chlorine produced at the anode and the hydrogen and caustic alkali produced at the cathode is prevented by means of a diaphragm. In mercury cells, the cathode consists of liquid mercury, which forms an amalgam with the alkali metal. This amalgam is removed from the cell and reacted with water in a denuder to give alkali hydroxide and hydrogen.

In the spent brine process the brine flows once through the cell, with the weak brine effluent leaving the cell then being discharged to waste. Alternatively, in the resaturation process, the weak brine is resaturated with solid salt and recirculated to the cell.

3.4.2. Sources of pollution

Both types of cell are liable to give rise to discharges of chlorine to the atmosphere. The major sources of chlorine include the vent gases from chlorine liquefaction, loading and unloading, and storage and process transfer tanks. Chlorine can be recovered by absorption into water or carbon tetrachloride in packed or spray towers, the efficiency of recovery being 97% or greater, depending on the concentration of chlorine in the vent gas.

Mercury cells also give rise to mercury-containing discharges. The main sources of atmospheric mercury containing discharges are the hydrogen by-product stream, the ventilation air from the inlet and outlet end-boxes of the cells, and the cell-room ventilation air. The first two of these can be cooled in order to precipitate out most of the mercury. This is done sometimes with water in a direct-contact cooler or packed tower, and the residual mercury mist removed by means of a mist eliminator.

Alternatively, activated carbon impregnated with iodine or sulfur can be used to react chemically with the mercury. A molecular sieve adsorption system has also been developed to remove mercury from the hydrogen and end-box streams. It is impracticable to remove mercury from cell-room ventilation air because of the large volumes of air involved and the only feasible control method is to prevent mercury vapour from entering the cell-room atmosphere.

Where the spent brine process is used, spent brine contaminated with mercury is discharged to waste, sometimes directly into waterways or the sea. However, the bulk of the mercury is usually first removed in treatment plants in an ion exchange process, or precipitated in canals as mercuric sulfide.

Sludges such as canal dredgings are usually disposed of in lagoons, while effluent treatment plant sludges are disposed of to appropriate landfill sites. Bulky solid mercury-bearing wastes (e.g., graphite anodes, concrete cell covers) have also been disposed of to landfill. Mercury-laden resin from ion-exchange treatment has been mixed with concrete and also disposed of to landfill.

Mercury-containing wastes can, of course, be completely eliminated by converting all mercury cells to diaphragm cells.

3.4.3. Discharge standards

Canada

The Chlor-Alkali Mercury National Emission Standards Regulations, made under the Clean Air Act, were promulgated by the Ministry of Fisheries and the Environment on 6 July 1977. These Regulations lay down the emission standards for chlor-alkali manufacture shown in Table 4A.

Table 4A: Emission standards for mercury discharges into the ambient air from
chlor-alkali manufacture (Canada)

Source of mercury	Maximum mercury emission (g/day per 1000 kg of rated capacity)
Cell-room ventilation air	5
Hydrogen stream from denuders	0.1
Ventilation air from end-boxes and tanks	0.1
Air exhausted from retorts	0.1

As from 1 July 1978, however, direct emissions of mercury from tanks were prohibited. In addition, as from the same date, the total amount of mercury emitted by the sources listed in Table 4A was not to exceed 1.68 kg/day.

The Regulations require the submission, if requested by the Minister, of regular emission measurement reports at intervals not exceeding three months. The Minister can also request reports on malfunctions or breakdowns, or on controls, as well as samples of gas streams emitted into the ambient air.

For liquid mercury-containing effluents, the Chlor-Alkali Mercury Liquid Effluent Regulations of 12 July 1977 (made under the Fisheries Act, as amended in 1970) apply. These Regulations permit the discharge of such effluents provided that the amount of mercury discharged in any day does not exceed 0.00250 kg per tonne of chlorine, multiplied by the reference production rate of the plant concerned. Methods of calculating the reference production rate are given in the Regulations.

The Regulations require the owner of a plant to install sampling equipment, to take a composite sample every day, to analyse it, to measure and record the effluent flow-rate every day, and to calculate the actual amount of mercury discharged. A detailed report on the operation of the plant and, in particular, on the mercury balance, has to be sent to the Minister at monthly intervals. The method to be used for determining total mercury in chlor-alkali effluents is specified in the Regulations.

Germany (Federal Republic)

Emissions of mercury from chlor-alkali production are governed by the Technical Guide for Air Quality Control of 1974, made under the Federal Law of 28 August 1974 on the prevention of pollution. The limit specified is 3 g/ton of chlorine.

Japan

The control of mercury-containing industrial discharges in Japan is the responsibility both of the Environment Agency and of the Ministry of International Trade and Industry. Thus the Agency has laid down that the mercury content of industrial wastewaters must not exceed 50 mg of total mercury per 1000 tonnes of wastewater.

The Ministry, however, has adopted a different approach. As a first step, the complete recycling of all mercury-containing process water was ordered, and supposed to have been achieved by December 1973. Secondly, the replacement of all mercury cells by diaphragm cells was ordered with a completion date for this operation of March 1978.

For solid mercury-containing wastes, the Solid Waste Control Law lays down the following requirements for sludges and muds:

<u>Mercury content (mg/kg)</u>	<u>Permitted method of disposal</u>
0.005 or less	Landfill
More than 0.005	Mixing with concrete, if the leachate exceeds 0.005 mg/kg, the blocks must be embedded in larger blocks.

The dumping of mercury-containing sludges and muds at sea is permitted under the Ocean Contamination Law under the following conditions:

<u>Mercury content (mg/kg)</u>	<u>Permitted method of disposal</u>
0.005 or less	At depths of 3500 m or more
More than 0.005 but less than 2.0	Mixed with concrete, blocks may be dumped in areas with low currents and few fish, provided that leachate mercury content is less than 0.005 mg/kg

Sludges and muds with a mercury content exceeding 2 mg/kg must be treated or incinerated.

Sweden

The National Environment Protection Board has issued the following guidelines for emissions of mercury from chlor-alkali manufacture:

Ventilation air	1 g/ton of product
Hydrogen steam	0.5 g/ton of product

Over the past decade the chlor-alkali producing plants in Sweden have reduced the discharge of mercury to water by more than 99% and to the atmosphere by approximately 90%. The long-term policy of the National Environment Protection Board is to initiate a change towards mercury-free technology. Consequently, new plants have been built with the membrane and diaphragm process and the board expects all existing plants to convert their process into non-mercury technology within the next 5-7 years.

United Kingdom

No emission limits for the manufacture of chlor-alkali are laid down in the Health and Safety at Work etc. Act 1974. The Inspectorate, however, has fixed a presumptive limit for chlorine, i.e. a limit that the Inspectorate will normally accept as confirmation that "the best practicable means" are being used. Complete elimination of chlorine emission is stated to be the aim, but where this cannot be consistently achieved, emissions containing up to 75 ppm (V/V) ($= 0.023 \text{ g/m}^3$) may be acceptable, with a suitable chimney height.

The disposal of mercury-containing wastes to land is covered by a Code of Practice issued by the Department of the Environment in 1977. This states that the total non-alkyl mercury content of wastes before disposal to landfill should not normally exceed 2% by weight averaged out over each load. In addition, during landfill disposal, the objective should be not to exceed a mercury content of 4 mg per kg of fill material averaged out over 1000 m^3 . Where it is preferable for the mercury content to exceed 4 mg/kg, additional safeguards may be necessary.

United States of America

Under the Clean Air Act, a National Emission Standard for Hazardous Air Pollutants has been developed for chlor-alkali manufacture. Mercury is a hazardous pollutant and under the Act an emission standard of 2300 g/24 hours has been laid down by the US Environmental Protection Agency.

Under the Federal Water Pollution Control Act Amendments of 1972 and the Clean Water Act of 1977, the US Environmental Protection Agency has issued effluent standards and guidelines for the chlor-alkali product process of the inorganic chemical manufacturing industry.

The "best practicable control technology currently available" (BPT) limits for discharge into navigable waters that must be satisfied immediately by existing plants, as well as the "best available technology economically achievable" (BAT) limits that must be satisfied by 1 July 1984, are shown in Table 4B for both the mercury cell and diaphragm cell processes. The limits for new plants discharging into navigable waters are given in Table 4C. The limitations on existing and new plants discharging into publicly owned treatment works are given in Tables 4D and 4E respectively.

Table 4B: Effluent limitations for existing plants producing chlor-alkali and discharging into navigable waters (USA) (kg/1000 kg of product)

Characteristic	Effluent limitations			
	Max. for any 1 day		Max. ave. of daily values for 30 consec. days	
	BPT	BAT	BPT	BAT
<u>Mercury Cell Process</u>				
Total suspended solids	0.64	-	0.32	-
Mercury (total)	0.00028	0.00023	0.00014	0.00010
Residual Chlorine (total)	-	0.0032	-	0.0019
pH	6.0-9.0	-	6.0-9.0	-
<u>Diaphragm Cell Process</u>				
Total suspended solids	1.1	-	0.51	-
Copper (total)	0.018	0.012	0.0070	0.0049
Lead (total)	0.026	0.0059	0.010	0.0024
Nickel (total)	0.014	0.0097	0.0056	0.0037
Residual Chlorine (total)	-	0.013	-	0.0079
pH	6.0-9.0	-	6.0-9.0	-

Table 4C: Effluent limitations for new plants producing chlor-alkali
and discharging into navigable waters (USA) (kg/1000 kg of product)

Characteristic	Effluent limitations	
	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
<u>Mercury Cell Process</u>		
Total suspended solids	0.64	0.32
Mercury (total)	0.00023	0.00010
Residual Chlorine (total)	0.0032	0.0019
pH	6.0-9.0	6.0-9.0
<u>Diaphragm Cell Process</u>		
Total suspended solids	1.1	0.51
Lead (total)	0.0047	0.0019
Residual Chlorine (total)	0.017	0.0079
pH	6.0-9.0	6.0-9.0

Table 4D: Effluent limitations for existing plants producing chlor-alkali through the diaphragm cell process and discharging into publicly-owned treatment works (USA)
(mg/litre) (a)

Characteristic	Effluent limitations	
	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Copper (total)	2.1(0.018)	0.80(0.0070)
Lead (total)	2.9(0.026)	1.1 (0.010)
Nickel (total)	1.6(0.014)	0.64(0.0056)

- (a) Where publicly - owned treatment works find it necessary to impose mass limitations on existing sources discharging process waste water to them, the limitations shown in brackets may be used.

Table 4E: Effluent limitations for new plants producing chlor-alkali and discharging into publicly-owned treatment works (USA) (mg/litre) (a)

Characteristic	Effluent limitations	
	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Mercury Cell Process Mercury (total)	0.11	0.48
DiaphragmCell Process Lead (total)	0.53(0.53)	0.21(0.21)

- (a) Where publicly - owned treatment works find it necessary to impose mass limitations on new sources discharging process waste water to them, the limitations shown in brackets may be used.

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3.5. FERTILIZERS

Fertilizers are chemical compounds containing one (straight fertilizers) or more (compound fertilizers) of the primary plant nutrients, nitrogen, phosphorus and potassium. They are manufactured from materials such as ammonia, nitric acid, sulfuric acid and phosphoric acid. The production of these materials will not be considered here.

3.5.1. Outline of process

Fertilizers can be divided into the following categories: superphosphates (single and triple); ammonium nitrate; ammonium sulfate; ammonium phosphate; urea; granular compound fertilizers; and potash fertilizers.

Single superphosphate (SSP) is produced by reacting ground phosphate rock with sulfuric acid in a cone, from which the resulting slurry is discharged on to a slowmoving conveyor; this carries the material to a den, where it quickly solidifies. Curing for 2-6 weeks follows and allows the chemical reactions to proceed to completion. In contrast, triple superphosphate (TSP) is produced by reacting ground phosphate rock with phosphoric acid. Both the rate of reaction and the rate of solidification are slower than for SSP.

Ammonium nitrate is produced by neutralizing nitric acid with ammonia. Ammonium sulfate can be made either by reacting ammonia with sulfuric acid, or calcium sulfate with ammonium carbonate. Ammonium phosphate is generally produced by neutralizing phosphoric acid with ammonia.

Urea is made by reacting ammonia with carbon dioxide at high temperatures and pressures.

The raw materials used for the manufacture of granular compound fertilizers will depend on the specific formulation desired. The manufacturing process involves the controlled addition of the raw materials to a granulator, which is often a rotary drum.

Potash fertilizers include a number of potassium salts, but 90% of world potash supply is in the form of potassium chloride derived from the mineral sylvite.

3.5.2. Sources of pollution

Since the phosphate rock used for the manufacture of superphosphates contains 4.5% of fluorine, large quantities of fluorides are released during the production process. These are generally removed by wet scrubbing; the scrubber effluents have then to be neutralized with lime.

Ammonium nitrate production gives rise to emissions of ammonia, nitric acid and ammonium nitrate. These may be removed by scrubbing. On the other hand, in the production of ammonium sulfate, the only emissions are those due to accidental escapes of ammonia. Ammonia losses are, however, considerable in the production of diammonium phosphate, and are dealt with by scrubbing with phosphoric acid; gaseous emissions containing fluorides may then be released, but can be removed by further scrubbing.

Urea dust from the prilling towers is the main atmospheric emission in the manufacture of urea, but can be removed by wet scrubbing. Wastewaters containing ammonia, carbon dioxide, ammonium carbonate and urea are produced when urea solutions are concentrated by flash evaporation.

Granular compound fertilizers are produced in a two-stage process involving a wet stage, consisting of a reactor and a neutralizer, and a dry stage, consisting of a granulation loop. Emissions from the wet stage are usually scrubbed with acid to remove ammonia and then further scrubbed to remove fluorides, nitrogen oxides and dust. Scrubbing gives rise to waste-waters, which are passed to a retention pond so as to allow insoluble solids to settle out. Dust emitted during granulation may be removed by means of cyclones, bag filters, tube filters or wet scrubbers.

3.5.3. Discharge standards

India

The tolerance limits for effluents from the manufacture of phosphatic and nitrogenous fertilizers are specified in Indian Standard IS:2490, part VIII (1976) and part IX (1977) respectively. These limits are shown in Tables 5A and 5B and, although not having the force of law, have been adopted and enforced by many of the State Boards responsible, under the Water (Prevention and Control of Pollution) Act, 1974, for establishing standards for trade effluents.

Table 5A: Tolerance limits for effluents from the manufacture of phosphatic fertilizers discharged into inland surface waters (India)

Characteristic	Tolerance limit
Dissolved phosphates (as P)(mg/litre)	5
Dissolved fluorides (as F)(mg/litre)	15
pH	5.5 - 9

Table 5B: Tolerance limits for effluents from the manufacture of nitrogenous fertilizers discharged into inland surface waters (India)

Characteristic	Tolerance limit
Ammoniacal nitrogen (as N)(mg/litre)	100
pH	5.5 - 9.5
Arsenic (as As)(mg/litre) new plant	0.2
Arsenic (as As)(mg/litre) existing plant	0.1
Free ammonia (as NH ₄)(mg/litre)	5.0

Japan

Article 5 of the Law of 1968 on air pollution control, as amended, specifies an emission standard of 15 - 20 mg/Nm³ for fluorine from the manufacture of superphosphate.

United Kingdom

Chemical manure works, i.e., works for the manufacture of superphosphates, and works for the granulating of chemical manures, are included in the List of Scheduled Works under the Alkali Act 1906.

Information on best practicable means for chemical fertilizer works has been published by the Inspectorate. In the manufacture of superphosphates the total acidity of discharge is not to be more than 0.23 g/m³. Alternatively, efficiency of absorption of acid gases must be greater than 99%. In the manufacture of granulated fertilizers, hydrogen chloride emission must not be more than 0.46 g/m³. While these limits do not have the force of law, they are the maximum that will normally be accepted as confirmation that the best practicable means are being used.

United States of America

Under the Clean Air Amendments of 1970, the Federal Government is empowered to issue performance standards for new stationary sources. The US Environmental Protection Agency has promulgated the standards listed in Tables 5C to 5E for the emission of air pollutants from the fertilizer manufacture industry.

Table 5C: Standards for total fluoride emissions from
new fertilizer plants (USA) (mg/litre)

Source	Pollutant	Emission level	Monitoring requirement
Wet process phosphoric acid	Total fluorides	10g/mg P_2O_5	No requirement Mass flow rate daily equivalent P_2O_5 feed, total pressure drop across scrubbing system
Superphosphoric acid	Total fluorides	5g/mg P_2O_5	No requirement Mass flow rate daily equivalent P_2O_5 feed, total pressure drop across scrubbing system
Granular triple super-phosphate storage	Total fluorides		No requirement Mass flow rate daily equivalent P_2O_5 feed, total pressure drop across scrubbing system
Diammonium phosphate	Total fluorides	30g/mg P_2O_5	No requirement Mass flow rate daily equivalent P_2O_5 feed, total pressure drop across scrubbing system
Triple superphosphate	Total fluorides	100g/mg P_2O_5	No requirement Mass flow rate daily equivalent P_2O_5 feed, total pressure drop across scrubbing system

Table 5D: Standards for emissions from phosphate rock plants (USA)

Source	Pollutant	Emission level	Monitoring requirement
Facilities with production capabilities 4 tons/h (3.6 mg/h):			
Dryer	Particulate	0.03 kg/mg feed	No requirement
Calciner			
Unbeneficiated or blend	Particulate	0.12 kg/mg feed	No requirement
Beneficiated	Particulate	0.055 kg/mg feed	No requirement
Dryer and calciner	Opacity	10%	Continuous, except when using wet scrubber
Grinder	Particulate	0.006 kg/mg feed	No requirement
	Opacity	0%	Continuous, except when using wet scrubber
Ground rock handling and storage	Opacity	0%	No requirement
Exempt: production or preparation for elemental phosphorus production			Wetscrubber: pressure loss and liquid supply pressure Feed rate to dryer calciner, and grinder

Table 5E: Standards for emissions from ammonium sulfate plants (USA)

Source	Pollutant	Emission level	Monitoring requirement
Ammonium sulfate dryer in caprolactum by-product, synthetic and coke oven by-product sectors	Particulate	0.15 kg/mg	No requirement
	Opacity	15%	No requirement
			Mass flow rate or weigh scales for production rate; total pressure drop across control system

Under the Federal Water Pollution Control Act Amendments of 1972 and the Clean Water Act of 1977, the US Environmental Protection Agency has issued effluent standards and guidelines for process wastewaters from the fertilizer manufacturing point source category. These standards and guidelines cover both existing and new facilities. Existing facilities were required to meet the "best practicable technology currently available" (BPT) standards by 1 July 1977 and will be required to meet the "best available technology economically achievable" (BAT) standards by 1 July 1984. New facilities must meet "new source performance standards" (NSPS) and, if discharging process wastewater into publicly-owned treatment works, must meet "pretreatment standards for new sources" (PSNS).

Effluent standards and guidelines cover production in the following subcategories:

Phosphate - Effluent standards and guidelines in this category apply to process wastewater discharges resulting from the manufacture of single superphosphate, triple superphosphate, ammonium phosphate, wet process phosphoric acid and sulfuric acid by sulfur burning. Limitations in this subcategory are shown in Table 5D. In this case BPT, BAT and NSPS standards are the same.

Phosphate manufacturing facilities are not generally allowed to discharge process wastewater pollutants into navigable waters. However, existing facilities are permitted to discharge effluents from a calcium sulfate storage pile runoff facility operated separately or in combination with a water recirculation system. Such discharge is allowed whenever chronic or catastrophic rainfall causes the water level to rise into the surge capacity. Under BPT, a surge capacity equal to the runoff from the maximum 24-hour rainfall with a probable recurrence of 10 years must be maintained to permit such discharge. Under BAT and NSPS a surge capacity equal to the runoff from the maximum 24-hour rainfall with a probable recurrence interval of 25 years must be maintained to permit such discharge. Any such discharge must be treated to the BPT effluent limitation given in Table 5F with the proviso that the total suspended solids limitation may be waived under certain conditions if the other limitations are met.

Table 5F: Effluent limitations for existing and new plants
producing phosphate (USA) (mg/litre)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Total phosphorus (as P)	105.0	35.0
Fluoride	75.0	25.0
Total suspended solids	150.0	50.0

Urea - The limitations imposed on existing plants under BPT standards are listed in Table 5G. Those to be met by existing plants under BAT standards, and those to be met by new sources discharging either to navigable waters (NSPS) or to publicly-owned treatment works are given in Table 5H.

Table 5G: BPT Effluent limitations for existing plants producing
urea (USA) (kg/1000 kg of product)

Plant	Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Manufacturing urea as a solution product	Ammonia (as N)	0.95	0.48
	Organic nitrogen (as N)	0.61	0.33
Manufacturing urea as prilled or granulated products	Ammonia (as N)	1.18	0.59
	Organic nitrogen (as N)	1.48	0.80

Table 5H: BAT, NSPS and PSNS effluent limitations for existing and new plants producing urea (USA) (kg/1000 kg of product)

Plant	Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Manufacturing urea as a solution product	Ammonia (as N)	0.53	0.27
	Organic nitrogen (as N)	0.45	0.24
Manufacturing urea as prilled or granulated products	Ammonia (as N)	0.53	0.27
	Organic nitrogen (as N)	0.86	0.46

Ammonium nitrate - The limitation under BPT for existing plants producing ammonium nitrate in any form are shown in Table 5I. The BAT limitations on existing plants and the NSPS and PSNS limits for new plants are given in Table 5J.

Table 5I: BPT effluent limitations for existing plants producing ammonium nitrate (USA) (kg/1000 kg of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Ammonia (as N)	0.73	0.39
Nitrate (as N)	0.67	0.37

Table 5J: NSPS and PSNS effluent limitations for existing and new plants producing ammonium nitrate (USA) (kg/1000 kg of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Ammonia (as N)	0.08	0.04
Nitrate (as N)	0.12	0.07

Ammonium sulfate - Process wastewaters resulting from the manufacture of ammonium sulfate by the synthetic process or by coke oven by-product recovery may not be discharged into navigable waters. There is a limit of 30 mg/litre for ammonia (as N) for wastewaters discharged from a new plant to a publicly owned treatment plant.

Mixed and blend fertilizer production - There must be no discharge of process wastewater pollutants to navigable waters, whether from existing or from new plants. The following limits apply to waste waters discharged from a new plant to a publicly-owned treatment plant

Ammonia (as N) 30 mg/litre
Total phosphorus (as P) 35 mg/litre

Ammonia - Effluent standards applying under BPT and BAT limitations to existing plants manufacturing ammonia are shown in Table 5K standards applying to new sources under NSPS and PSNS are shown in Table 5L.

Table 5K: Effluent standards applying to existing plants producing ammonia (USA) (kg/1000 kg of product)

Characteristic	Max. for any 1 day		Max. ave. of daily values for 30 consec. days	
	BPT	BAT	BPT	BAT
Ammonia (as N)	0.1875	0.05	0.0625	0.025
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

Table 5L: PSNS and NSPS effluent standards applying to new plants producing ammonia (USA) (kg/1000 of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Ammonia (as N)	0.11	0.055
pH	6.0-9.0	6.0-9.0

Nitric acid - Effluent standards and guidelines apply to process waste water discharges resulting from the manufacture of nitric acid in concentrations up to 68%. A distinction is made for existing facilities between facilities using liquid or gaseous ammonia as a feedstock. Limits applying to existing plants under BPT and BAT are shown in Table 5M. Those applying to new plants under NSPS and PSNS are shown in Table 5N.

Table 5M: Effluent standards applying to existing plants producing nitric acid (USA) (kg/1000 of product)

Plant	Characteristic	Max. for any 1 day		Max. ave. of daily values for 30 consec. days	
		BPT	BAT	BPT	BAT
Using gaseous ammonia feedstock	Ammonia (as N)	0.007	0.0045	0.0007	0.00045
	Nitrate (as N)	0.33	0.17	0.044	0.023
Using liquid ammonia feedstock	Ammonia (as N)	0.08	0.08	0.008	0.008
	Nitrate (as N)	0.33	0.17	0.044	0.023

Table 5N: PSNS and NSPS effluent standards applying to new plants
producing nitric acid (USA) (kg/1000 kg of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Ammonia (as N)	0.0045	0.00045
Nitrate (as N)	0.17	0.023

3.5.4 References

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3.6. HYDROCHLORIC, NITRIC AND SULFURIC ACIDS

The three acids, hydrochloric, nitric and sulfuric, are among the most important inorganic chemicals to be produced on a large scale.

3.6.1. Outline of process

Hydrochloric acid is produced mainly as a by-product of the chlorination of organic compounds. The remainder is produced either by the reaction between sodium chloride and sulfuric acid (salt process) or by direct combination of hydrogen and chlorine.

Nitric acid can be produced by the pressure process, in which air and ammonia are passed through a catalyst bed at high temperature and pressure to give nitrogen monoxide. This is then oxidized to form nitrogen dioxide and dinitrogen tetroxide, which are absorbed in dilute nitric acid to give 50-70% acid. Further concentration to give 98% acid can be achieved by addition of concentrated sulfuric acid and distillation of the mixture. Alternatively, in the direct strong acid process, ammonia is oxidized to form dinitrogen tetroxide, which is condensed by refrigeration and autoclaved together with water or weak acid and oxygen to give 98% acid.

Sulfuric acid is now produced mainly by the contact process. This involves the catalytic conversion of sulfur dioxide, usually produced by burning sulfur, into sulfur trioxide, which is then absorbed in strong sulfuric acid.

3.6.2. Sources of pollution

In all processes for the manufacture of hydrochloric acid, the hydrogen chloride gas is absorbed in water or weak acid. The tail gases from the absorbers used for this purpose account for most of the losses of hydrogen chloride.

In nitric acid manufacture, the tail gas streams from weak acid manufacture constitute the main source of emissions, these consist mainly of nitrogen monoxide and nitrogen dioxide. Such emissions can be controlled by catalytic reduction, adsorption or absorption.

The exhaust gases from the acid absorption tower constitute the main source of emissions of sulfur dioxide and acid mists in sulfuric acid manufacture. The sulfur dioxide can be removed by scrubbing, e.g., with ammonia liquor or hydrogen peroxide. Mist emissions can be controlled by means of fibre demisters in conjunction with electrostatic precipitators, or most effectively with high-efficiency tubular demisters.

3.6.3. Discharge standards

Australia

The Australian National Health and Medical Research Council recommends National Emission Standards for Air Pollutants. These standards are recommended to Statutory Authorities as considered opinion on the concentrations which can be realised by the use of the "best practicable technology" and to which all new plants and installations should be designed. These standards are being incorporated progressively into regulations enacted by state governments for new plants. The recommended standards for acids are shown in Table 6A.

Table 6A: Standards for atmospheric emissions: manufacture of acids (Australia)

Substance	Source	Standard
Hydrogen sulfide	Any trade industry or process	5 mg/m ³
Sulfuric acid mist and sulfur trioxide	Any trade industry or process	0.1 g/m ³ expressed as SO ₃
Nitric acid or oxides of nitrogen	Nitric acid plants	2.0 g/m ³ expressed as NO ₂
	Sulfuric acid plants	1.0 g/m ³ expressed as NO ₂
	Any trade industry or process except nitric or sulfuric acid plants or gas fired power stations	0.5 g/m ³ expressed as NO ₂
Oxides of nitrogen	Gas fired power stations	0.35 g/m ³ expressed as NO ₂

France

A Circular of 31 July 1974 specifies that, under normal conditions, the exit gases from nitric acid factories must not contain more than 4.5 kg/ton of 100% acid, averaged over a 2-hour period. To allow for exceptional circumstances, the acid content is permitted to exceed this figure, but not for more than 48 hours during any one continuous period, or for more than a total of 400 hours in any one year. In no case must the nitrous acid content of the gases exceed 6 kg/ton of 100% acid.

Germany (Federal Republic)

Limitations on emissions from the manufacture of all three acids are given in the Technical Guide for Air Quality Control of 1974, made under the Federal Law of 28 August 1974 on the prevention of pollution. The limitations are shown in Table 6B.

Table 6B: Standards for atmospheric emission: manufacture of acids (FRG)

Substance	Standards
Hydrochloric acid (by direct combination)	10 mg/Nm ³
Nitric acid	1-2 g/Nm ³ (the plume must be colourless)
Sulfuric acid: SO ₂ content 6-8% by volume; conversion efficiency greater than 99%	0.4 kg/1000 kg of SO ₃
SO ₂ content less than 6% by volume; conversion efficiency greater than 97%	0.6 kg/1000 kg of SO ₃

Japan

Article 3 of the Law of 1968 on air pollution control, as amended, specifies an emission standard of 80 mg/Nm³ for hydrogen chloride.

Sweden

The National Environment Protection Board has issued the following guidelines for emissions from sulfuric acid factories:

sulfur dioxide 5 kg/1000 kg acid

United Kingdom

Works for the manufacture of hydrochloric acid, nitric acid, and sulfuric acid are included in the List of Scheduled Works under the Alkali Act 1906. The Health and Safety at Work etc. Act 1974 also contains two statutory limits for emissions from these works. In addition, the Inspectorate has fixed "presumptive limits", i.e. limits that will be normally accepted as confirmation that "the best practicable means" are being used. The limitations for acids are shown in Table 6C.

Table 6C: Standards for atmospheric emissions: manufacture of acids (United Kingdom)

Substance	Statutory limit	Presumptive limit
Hydrogen chloride	0.46 g/m ³	-
Nitric acid	-	nitrogen oxides - 1000 ppm (V/V)
Sulfuric acid (all new contact plants)	-	Sulphur loss to air, as acid gases: 0.5% of sulphur burned.
Sulfuric acid concentration and distillation	Total acidity - 3.45 g/m ³	-

United States of America

Under the Clean Air Amendments of 1970, the US Environmental Protection Agency has promulgated standards for new and modified sulfuric and nitric acid plants as shown in Table 6D.

Table 6D: Emission standards for new sulfuric and nitric acid plants (USA)

Source	Pollutant	Emission level	Monitoring requirement
Nitric Acid Plants Process equipment	Opacity	10%	No requirement
	NO _x	1.5 kg/mg	Continuous Daily production rates and hours
Sulfuric Acid Plants Process equipment	SO ₂	2 kg/mg	Continuous
	Acid mist	0.075/kg/mg	No requirement
	Opacity	10%	No requirement

Water effluent standards and guidelines have not been developed for the hydrochloric, nitric and sulfuric acid product processes as pollutant concentrations and toxicities observed in effluent samples have been judged not to justify the development of national regulations.

3.6.4. References

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3.7. INDUSTRIAL ORGANIC CHEMICALS

Industrial organic chemicals include a wide range of compounds, often derived from petrochemicals. Many of these compounds are used as intermediates in the production of plastics, synthetic fibres, dyestuffs, pharmaceuticals and surfactants.

3.7.1. Outline of process

Because of the very large number of compounds produced, a wide variety of processes is used, including esterification, saponification, oxidation, sulfonation, chlorination, nitration, condensation, reduction, dehydrogenation, etc. These cannot be considered in detail here.

3.7.2. Sources of pollution

The major pollution problem from organic chemical plants is through pollutants contained in wastewater. Such wastewaters may be contaminated with raw materials used, intermediates, finished products or possibly toxic by-products, e.g., sulfides from sulfonations, cyanides from the manufacture of acrylonitrile, phenols, etc. Other contaminants include oils, suspended solids and catalysts.

Cyanides can be removed by oxidation with chlorine or persulfuric acid. Phenols can be subjected to complete chemical oxidation, adsorbed on to activated carbon, removed by solvent extraction, or treated biologically. Suspended matter can be settled out with the aid of a flocculating agent.

3.7.3. Discharge standards

India

The tolerance limits for effluents from the manufacture of dyestuffs and dye intermediates, discharged into inland surface waters, are specified in the Indian Standard IS:2490, part VI, (1976); these are shown in Table 7A. These limits do not have the force of law, but have been adopted and enforced by many of the State Boards responsible, under the Water (Prevention and Control of Pollution) Act, 1974, for the control of water pollution, and in particular for establishing standards for trade effluents.

The standard is based on those effluent treatment techniques considered to be technologically and economically suitable for adoption in India. It is expected to be reviewed in 1981, when improved treatment techniques are likely to be both available and within the economic capability of the industry.

Table 7A: Tolerance limits for effluents from the manufacture of dyestuffs and dye intermediates into inland surface waters (India)

Characteristic	Tolerance limit
pH	5.5 - 9.0
Suspended solids (mg/litre)	100
Zinc (as Zn) (mg/litre)	5

United States of America

Under the Federal Water Pollution Control Act Amendments of 1972, the US Environmental Protection Agency has issued effluent limitations for the organic chemicals manufacturing point source category. These apply solely to discharges of process waste water from the manufacture of butadiene by any process including the oxidative-dehydrogenation of butene. For existing plants, limitations are given for the "best practicable technology currently available" (BPT) and for the "best available technology economically achievable" (BAT). Of course, the BPT limitations must be satisfied immediately and the BAT limitations not later than July 1983; the latter also apply to new plants. The limitations are shown in Table 7B.

Table 7B: Effluent limitations for plants making butadiene by the oxidative-dehydrogenation of butene (USA) (kg/1000 kg of product)

Characteristic	Effluent limitations			
	Max. for any 1 day		Max. ave. for 30 consec. days	
	BPT	BAT	BPT	BAT
COD	-	7.8	-	4.2
BOD ₅	2.3	0.57	1.0	0.27
Total suspended solids	2.3	0.94	1.0	0.50
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

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3.8. IRON AND STEEL

The function of the iron and steel industry is essentially to convert iron ore first into iron and then into steel. The associated processes of extracting the ore, the finishing of steel products, and the production of special alloy steels will not be considered here.

3.8.1. Outline of process

Iron ore can be reduced by means of coke in a blast furnace to give pig iron. Direct reduction with a gaseous reducing agent can also be used to yield high-purity sponge iron. As little information is available on pollution problems associated with direct reduction, and reduction in a blast furnace is still the major route, this section will therefore deal with blast furnace ironmaking only.

For use in the blast furnace, coal of appropriate quality must first be converted into metallurgical coke in coke ovens. In addition, the iron ore has to be sintered or pelletized so as to convert it into a form suitable for charging into the blast furnace. In steelmaking, the carbon content of the pig iron produced in the blast furnace is reduced and undesirable impurities removed; various types of furnace may be used for this purpose.

3.8.2. Sources of pollution

Coking - Coal is converted into coke in batteries of coke ovens. In these batteries, it is heated in the absence of air to a temperature at which most of the volatile matter, water and sulfur are driven off. The coke is then discharged and quenched with water, after which the cycle is repeated. About 60% of total coke plant particulate emissions are accounted for by coke oven charging, and about 30% by discharging. Quenching gives rise to steam containing dust and water droplets; it also produces highly contaminated waste water. Particulate emissions from coking can be reduced by various process modifications or by the use of gas scrubbers. Biological oxidation processes can be used for the treatment of wastewater from quenching.

Ore preparation - In sintering, the moist ore is mixed with finely divided coke breeze and fluxes, and the mixture transferred to a permeable travelling grate. It is then ignited, and air is drawn through it into a series of distribution chambers (windboxes). A fused mass (sinter) is formed, which is cooled, crushed and screened to give a suitable blast furnace feed.

The windbox waste gases contain entrained dust particles together with carbon monoxide, sulfur oxides, and volatilized contaminants. The dust can be removed by means of gravity settlers followed by mechanical collectors. Wet scrubbers can also be used; these will, in addition, remove sulfur oxides. Other dust emissions can arise when sinter is broken up and screened, and in the course of materials handling.

Pelletization produces only very small amounts of dust.

Pig iron production (ironmaking) - The pellets or sinter, together with coke and fluxes, are charged into the top of the blast furnace, while heated air is injected under pressure at the bottom. The ore descends through the furnace and is reduced, mainly by carbon monoxide produced by the partial combustion of the coke. Molten iron is tapped from the bottom of the furnace while blast-furnace gas leaves from the top.

Dust is discharged with the blast-furnace gas, which is therefore passed through a multistage collection system. Tapping (casting) is also a source of particulates; these can be removed by means of fabric filters. Blast-furnace gas washing waters have a high suspended solids content, and may also contain cyanide. The solids are usually separated by settlement and thickening, while cyanides can be removed by aeration and biological filtration.

Steelmaking - Pig iron is converted into steel by the oxidation of most of the carbon which it contains; this is now usually accomplished by the use of oxygen. Three main types of furnace are used in steelmaking.

In the traditional open-hearth furnace, preheated air plus fuel are blown into the furnace at one end and exhaust gases withdrawn at the other. Oxygen lancing may be used to increase the production rate. Dust is emitted during furnace operation, and amounts are greatly increased if oxygen lancing is employed. The dust can be removed by means of electrostatic precipitators together with high-energy scrubbers.

In the electric-arc furnace, the charge is melted by the passage of a current through it from one electrode to the other. Oxygen lancing may be used to increase the production rate, although this results in increased particulate emissions from the furnace. Wet scrubbers can be used for dust removal.

Various types of basic oxygen furnace are used, in all of which the temperatures reached may be high enough for appreciable amounts of iron to be volatilized. Subsequent cooling and

oxidation then gives rise to a fine brown fume of iron oxide particles. These can be removed by means of electrostatic precipitators, bag filters and high-energy scrubbers. Emissions also occur during hot metal transfer, charging and tapping; the particulates discharged can be removed by means of fabric filters or wet scrubbers. Where a wet method of fume cleaning is used, the washing water may contain high concentrations of solids; these can be removed by sedimentation and filtration.

3.8.3. Discharge standards

Canada

The Department of the Environment issued National Emission Guidelines for the metallurgical coke manufacturing industry in 1975 as shown in Table 8A.

Table 8A: Emission guidelines for the metallurgical coke manufacturing industry (Canada)

Source	Emission Guideline
Charging	100 g/metric ton of dry coke
Pushing	0.46 g/Nm ³
Quenching	50 g/metric ton of dry coke
Crushing and screening	0.046 g/Nm ³ (downstream of gas cleaning equipment)
Battery stacks	0.069 g/Nm ³ (in exhaust gases)
Burning of coke oven gas	1300 g SO ₂ /metric ton of dry coke

France

Circulars on iron ore sinter plants and steelworks using oxygen lancing were issued by the Minister for the Protection of Nature and the Environment on 24 July 1972 and 8 March 1973 respectively. They apply to all new plants and to existing plants undergoing major modifications. In addition, they are intended to serve as models for existing plants about which complaints have been made. They were drawn up by working parties consisting of representatives of government, industry, manufacturers of pollution-control equipment, etc.

Iron ore sinter plants - Under normal conditions, the particulate content of the gases discharged to the atmosphere must not exceed 0.150 g/Nm³. To allow for exceptional circumstances, a particulate content of up to 0.5 g/Nm³ is permitted, but not for more than 200 hours per year.

Steelworks using oxygen lancing - The gases discharged must not show any marked coloration, and the particulate content must not exceed 0.120 g/Nm³. Where for some reason the particulate content cannot be reduced to this level, no new batch of metal may be refined until the gas-cleaning equipment is again operating with the required efficiency. Exceptionally, however, refining may be allowed to continue for a limited period if the plant upstream of the process cannot be stopped without danger to the equipment or the operating personnel.

Germany (Federal Republic)

Emissions from iron and steel manufacture are governed by the Technical Guide for Air Quality Control of 1974, made under the Federal Law 28 August 1974, on the prevention of pollution, as follows:

Coking plants - The gas used for heating the coke must not contain hydrogen sulfide at an hourly mean concentration exceeding 1.5 g/m³ or other sulfur compounds at an hourly mean concentration of more than 0.5 g/m³. In the charging of the ovens, a dust removal efficiency of at least 90% must be achieved. The optical density of the smoke emitted may exceed the generally applicable limit of Ringelmann 2, but only for short periods.

Iron ore sintering plants - Gaseous effluents must not contain more than 5 g/m³ of inorganic fluorine compounds (expressed as fluoride ion).

Blast furnaces - The dust content of the waste gases must not exceed 20 mg/m³, or 50 mg/m³ if the gases are flared. There is no restriction on the sulfur content of the fuel, provided that the sulfur is removed by the slag.

Steelmaking furnaces - The dust content of the waste gases must not exceed 150 mg/m³. Carbon monoxide must be used, burned or dispersed.

Japan

The ordinances made under the Law of 1968 on air pollution control lay down limiting values for dust emissions from iron and steel manufacture, as shown in Table 8B.

Table 8B: Iron and steel manufacture: emission standards for dust (Japan)

Type of plant	General emission standard (g/Nm ³)	Standard for special areas (g/Nm ³)
Blast furnaces	0.10	0.05
Converters, open-hearth furnaces, sinter plants		
•emissions of less than 40 000 Nm ³ /h	0.40	0.20
•emissions of 40 000 Nm ³ /h and greater	0.30	0.20
Electric steel furnaces		
•emissions of less than 40 000 Nm ³ /h	0.40	0.20
•emissions of 40 000 Nm ³ /h and greater	0.20	0.10

Sweden

The National Environment Protection Board has issued the following guidelines, expressed as monthly averages, for particulate emissions in iron and steel manufacture:

Table 8C: Guidelines for particulate emissions in iron and steel manufacture (Sweden)

Type of plant	Emission guideline
Blast furnaces	0.3 kg/ton
Basic oxygen furnaces	0.3 kg/ton
Sinter plants:	
existing	1.0 kg/ton
new	0.5 kg/ton
Electric arc furnaces:	
existing	0.6 kg/ton
new	0.3 kg/ton
Miscellaneous operations	20-50 mg/Nm ³ dry gas (a)

(a) in practice; no official guideline

United Kingdom

Iron and steel works are included in the List of Scheduled Works under the Alkali Act 1906. Information on best practicable means for iron and steel works has been published by the Inspectorate, and certain particulate emission limits specified, as shown in Table 8D. While these limits do not have the force of law, they are the maximum that will normally be accepted as confirmation that the best practicable means are being used.

Table 8D: Particulate emission limits for iron and steel works (United Kingdom)

Source	Emission limit (g/m ³)
Ore preparation and sintering	0.115
Blast furnaces	0.46
Oxygen-using processes	0.115
Hot blast cupolas	0.115

Where no specific limits have been laid down, processes must be operated so as to minimize pollution; thus a code of practice for coke ovens has been published.

United States of America

Under the Clean Air Amendments, the Federal Government was empowered to issue performance standards for new stationary sources. The standards listed in Table 8E have been promulgated by the US Environmental Protection Agency for new iron and steel plants.

Table 8E: Performance standards for new iron and steel plants (USA)

Source	Pollutant	Emission level	Monitoring requirement
Basic oxygen process furnace	Particulate	50/mg/Nm ³	No requirement
	Opacity	10%(20% exception/cycle)	No requirement Time and duration of each cycle; exhaust gas diversion; scrubber pressure loss; water supply pressure
Electric arc furnace	Particulate	12 mg/Nm ³	No requirement
	Opacity (a) control device	3%	Continuous
	(b) shop roof	0% except ≤20%-charging ≤40%-tapping	Flow rate monitoring in capture hood, Pressure monitoring in DSE system
Dust handling equipment	Opacity	10%	No requirement

Under the Federal Water Pollution Control Act Amendments of 1972 and the Clean Water Act of 1977, the US Environmental Protection Agency issued limitations for waste waters from the iron and steel manufacturing industry. A thorough study of the industry showed that it consisted of a series of processes differing so greatly from one another as to require division into the following subcategories.

- | | |
|--------------------|-------------------|
| cokemaking | hot forming |
| sintering | scale removal |
| ironmaking | acid pickling |
| steelmaking | cold forming |
| vacuum degassing | alkaline cleaning |
| continuous casting | hot coating |

For each sub-category a number of sets of discharge limits have been established. Existing plants discharging to navigable waters are required to meet standards derived from the "best practical control technology" (BPT). For conventional pollutants (total suspended solids, oil and grease and pH) existing plants will be required to meet "best conventional technology" (BCT) limits by 1 July 1984. For non-conventional and toxic pollutants, existing plants will have to achieve limits derived from the "best available technology economically achievable" (BAT) by 1 July 1984. New plants discharging to navigable waters must achieve a performance defined by the new source performance standards (NSPS). Existing plants discharging to publicly-owned treatment works will be required to meet pretreatment standards for existing sources (PSES) by 27 May 1985, while new plants discharging to publicly owned treatment works are required to meet pretreatment standards for new sources (PSNS). The by-product cokemaking (iron and steel) sub-category has been selected to exemplify the prescribed limitations. These operations produce coke for use in iron blast furnaces by heating coal in the absence of air. The limitations applicable to this sub-category are given in Tables 8F to 8L.

Table 8F: BPT effluent limitations for existing by-product cokemaking
(iron and steel) plants discharging to navigable waters (USA) (kg/1000 of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Total suspended solids	0.253	0.131
Oil and grease	0.0327	0.0109
Ammonia - N	0.274	0.0912
Cyanide	0.0657	0.0219
Phenols (4AAP)	0.00451	0.00150
pH	6.0-9.0	6.0-9.0

- (1) Increased loadings, not to exceed 11 percent of the above limitations, are allowed for by-product coke plants which have wet desulfurization systems but only to the extent such systems generate an increased effluent volume.
- (2) Increased loadings, not to exceed 27 percent of the above limitations, are allowed by by-product coke plants which include indirect ammonia recovery systems but only to the extent that such systems generate an increased effluent volume.

Table 8C: BAT effluent limitations for existing by-product cokemaking
(iron and steel) plants without physical-chemical treatment systems discharging into
navigable waters (USA) (kg/1000 kg of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Ammonia - N	0.0543	0.0160
Cyanide	0.00638	0.00351
Phenols (4AAP)	0.0000638	0.0000319
Benzene	0.0000319	-
Naphthalene	0.0000319	-
Benzo(a)pyrene	0.0000319	-

- (1) Increased loadings not to exceed 16 percent of the above limitations, are allowed for by-product coke plants which have wet desulfurization systems but only to the extent such systems generate an increased effluent volume.
- (2) Increased loadings, not to exceed 39 percent of the above limitations, are allowed for by-product coke plants which include indirect ammonia recovery systems but only to the extent such systems generate an increased effluent volume.

Table 8H: BAT effluent limitations for existing by-product cokemaking (iron and steel) plants with physical-chemical treatment systems discharging into navigable waters (USA) (kg/1000 kg of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Ammonia - N	0.0645	0.0322
Phenols (4AAP)	0.0000859	0.0000430
Benzene	0.0000215	-
Naphthalene	0.0000215	-
Benzo(a)pyrene	0.0000215	-

- (1) Increased loadings, not to exceed 24 percent of the above limitations, are allowed for by-product coke plants with physical chemical treatment systems which have wet desulfurization systems but only to the extent such systems generate an increased effluent volume.

Table 8I: BCT effluent limitations for existing by-product cokemaking (iron and steel) plants discharging to navigable waters (USA) (kg/1000 kg of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Total suspended solids	0.253	0.131
Oil and grease	0.0321	0.0109
pH	6.0-9.0	6.0-9.0

- (1) Increased loadings, not to exceed 11 percent of the above limitations, are allowed for by-product coke plants which have wet desulfurization systems but only to the extent such systems generate an increased effluent volume.
- (2) Increased loadings, not to exceed 27 percent of the above limitations, are allowed for by-product coke plants which include indirect ammonia recovery systems but only to the extent that such systems generate an increased effluent volume.

Table 8J: NSPS effluent limitations for new by-product cokemaking (iron and steel) plants discharging to navigable waters (USA) (kg/1000 kg of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Total suspended solids	0.172	0.0894
Oil and grease	0.00638	-
Ammonia - N	0.0543	0.0160
Cyanide	0.00638	0.00351
Phenols (4AAP)	0.0000638	-
Benzene	0.0000319	-
Naphthalene	0.0000319	-
Benzo(a)pyrene	0.0000319	-
pH	6.0-9.0	6.0-9.0

- (1) Increased loadings, not to exceed 16 percent of the above limitations, are allowed for by-product coke plants which have wet desulfurization systems but only to the extent such systems generate an increased effluent volume.
- (2) Increased loadings, not to exceed 39 percent of the above standards, are allowed for by-product coke plants which include indirect ammonia recovery systems but only to the extent such systems generate an increased effluent volume.

Table 8K: PSES effluent limitations for existing by-product cokemaking (iron and steel) plants discharging to publicly-owned treatment works (USA) (kg/1000 kg of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Ammonia - N	0.0645	0.0322
Cyanide	0.0172	0.00859
Phenols (4AAP)	0.0430	0.0215

- (1) Increased loadings, not to exceed 24 percent of the above standards, are allowed for by-product coke plants which have wet desulfurization systems but only to the extent such systems generate an increased effluent volume.
- (2) Increased loadings, not to exceed 58 percent of the above standards, are allowed for by-product coke plants which include indirect ammonia recovery systems but only to the extent such systems generate an increased effluent volume.

Table 8L: PSNS effluent limitations for new by-product cokemaking (iron and steel) plants discharging to publicly-owned treatment works (USA) (kg/1000 kg of product)

Characteristic	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Ammonia - N	0.0645	0.0322
Cyanide	0.0172	0.00859
Phenols (4AAP)	0.0430	0.0215

- (1) Increased loadings, not to exceed 24 percent of the above standards are allowed for by-product coke plants which have wet desulfurization systems but only to the extent such systems generate an increased effluent volume.
- (2) Increased loadings, not to exceed 58 percent of the above standards, are allowed for by-product coke plants which include indirect ammonia recovery systems but only to the extent such systems generate an increased effluent volume.

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3.9. METAL FINISHING

A wide range of specialized metal finishing processes are used for protecting metals against corrosion, improving their properties or enhancing their appearance.

3.9.1. Outline of process

Before metal finishing processes can be carried out, pretreatment is usually necessary to remove natural oxide films, corrosion products, or protective oils and greases. The natural oxide films and corrosion products can be removed either by mechanical methods (brushing, descaling, polishing, shot blasting) or by chemical processes (acid pickling, sodium hydroxide descaling). Protective oils and greases may be removed by means of organic solvents.

Pretreatment may be followed by any of a number of processes. These may be grouped as follows:

- electroplating
- stripping
- chemical conversion (anodizing, phosphating, chromating)
- metal coating (galvanizing, rust-proofing sherardizing, peen plating, calorizing, metal spraying, hot-dip aluminizing, vacuum metallizing)
- machine (chemical, electrochemical, etching)
- final polishing
- case hardening
- other processes (electroforming, electroless plating)

3.9.2. Sources of pollution

Each individual process will be associated with specific sources of pollution and types of effluent. Thus, pretreatment by means of acid pickling prior to galvanizing will give rise to spent acid pickling liquors containing high concentrations of iron salts which, on neutralization, will produce insoluble hydroxides. Spent liquors from the pickling of copper and its alloys, however, will contain high copper concentrations with smaller amounts of zinc. Electroplating generally produces acid wastes containing dissolved copper, nickel and zinc, and occasionally chromium, cadmium or lead. Anodizing gives rise to a range of wastes, including both alkaline and acidic solutions, nitric acid and nitrates, phosphoric acid, chromium-bearing acidic solutions, bright anodizing solutions (nitric/phosphoric/acetic acids), and nickelbearing sealing solutions. Electrochemical machining produces electrolyte solutions (usually sodium nitrate and/or sodium chloride) and sludges, slurries and filter cake consisting of metallic oxides or hydroxides. Finally, one method of case hardening involves heat treatment by immersion of ferrous components in baths containing a mixture of molten cyanide, chloride and carbonate salts, these baths often contain barium as well. The wastes produced comprise discarded bath contents and ladlings, aqueous quench or rinse liquors, waste oil from oil quenching, and miscellaneous cyanide-containing wastes from spills, etc.

Because of the complexity of the wastes, there is no standard form of treatment, but chemical methods are generally used. These may include separation of alkaline cyanide-containing waste waters from acidic chromate-containing wastes, destruction of cyanides by oxidation with chlorine or hypochlorite, the use of sodium bisulfite or sulfur dioxide to reduce hexavalent chromium to the trivalent form, and precipitation of dissolved metals as hydroxides, basic carbonates or sulfides. The precipitated solids can then be separated as a sludge by gravitational settling in sedimentation tanks. Solid cyanide-containing wastes from heat-treatment processes may also be dumped at sea, buried in land, or incinerated.

3.9.3. Discharge standards

Canada

Guidelines on metal finishing liquid effluents were issued on 5 November 1977 under the authority of the Minister of Fisheries and the Environment. Stricter local or provincial requirements may be imposed where necessary. The aim of the Guidelines is to ensure that the "best practicable technology" is applied to the control of liquid effluents by all metal finishing plants operating in Canada. The effluent quality standards contained in the Guidelines reflect that technology and were based on the recommendations of a task force consisting of officials of federal and provincial regulatory agencies and industry representatives.

While not having the force of law, the Guidelines constitute a statement of the practices that will be considered by the Federal Government to meet the intent of the Fisheries Act, as amended in 1970.

For the purposes of the Guidelines, metal finishing is defined as comprising the following processes: electroplating, electroforming, anodizing, electrochemical machining, electrochemical polishing, electroless plating, chromating and cyanide hardening (case hardening with a molten cyanide salt). The Guidelines specify objectives for the quality of metal finishing liquid effluents as shown in Table 9A.

Table 9A: Quality objectives for metal finishing wastes (Canada)

Characteristic	Maximum value in any 1 day
Total suspended matter (mg/litre)	30
Cadmium (mg/litre)	1.5
Total chromium (mg/litre)	1.0
Copper (mg/litre)	1.0
Lead (mg/litre)	1.5
Zinc (mg/litre)	2.0
Nickel (mg/litre)	2.0
Oxidizable cyanide (mg/litre)	0.1
Total cyanide (mg/litre)	3.0
pH	6.0 - 9.5

Every owner of a metal finishing plant is required to install sampling and analytical equipment, to keep records and to send monthly reports to the Minister regarding the concentrations of the substances listed in Table 9A and the pH. The test methods to be used are specified in the Guidelines.

Germany (Federal Republic)

Guidelines for waste waters from the pickling of iron, galvanizing, anodic oxidation, and case hardening, after treatment, have been published by the Länderarbeitsgemeinschaft Wasser, and are shown in Table 9B.

Table 9B: Guidelines for discharges from metal finishing plants (FRG)

Characteristic	Recommended values after chemical treatment			
	Pickling of iron	Galvanizing	Anodic oxidation	Case hardening
Settleable solids (ml/litre)	0.3	0.3	0.3	0.3
pH	6.0-9.0	6.5-9.0	6.0-8.0	6.0-9.0
Total iron (mg/litre)	2	2	-	-
Total chromium (mg/litre)	-	2	2.0	-
Of which chromium VI (mg/litre)	-	0.5	0.5	-
Copper (mg/litre)	-	1	-	-
Nickel (mg/litre)	-	3	-	-
Zinc (mg/litre)	-	3	-	-
Cadmium (mg/litre)	-	3	-	-
Cyanide amenable to chlorination (mg/litre)	-	0.1	-	0.1
Free chlorine (mg/litre)	-	0.5	-	0.5
Petroleum ether extract (mg/litre)	-	10	-	10
Fluoride ion (mg/litre)	-	-	20	-
Nitrite ion (mg/litre)	-	-	-	20

India

The tolerance limits for electroplating effluents discharged into surface waters are specified in Indian Standard IS: 2490, part V (1974) and are shown in Table 9C. These limits do not have the force of law, but have been adopted and enforced by many of the State Boards responsible, under the Water (Prevention of Pollution) Act, 1974, for the control of water pollution, and in particular for establishing standards for trade effluents.

Table 9C: Tolerance limits for electroplating effluents discharged into inland surface waters (India)

Characteristic	Tolerance limit
Cadmium (as Cd) (mg/litre)	2.0
Nickel (as Ni) (mg/litre)	3.0
Zinc (as Zn) (mg/litre)	5
pH	7.0 - 9.0
Cyanides (as CN) (mg/litre)	0.2
Suspended solids (mg/litre)	30
Chromium VI (as Cr) (mg/litre)	0.1
Copper (as Cu) (mg/litre)	3

Italy

The Law of 10 May 1976 prescribing rules for the protection of waters against pollution contains limiting values for the acceptability of industrial effluents from new plants, depending on whether they are discharged into surface waters or into public sewers. The values relevant to metal finishing are shown in Table 9D.

Table 9D: Limiting values for acceptability of metal finishing discharges from new plants (Italy)

Characteristic	Limiting values for discharges into:	
	Surface waters	Public sewers
pH	5.5-9.5	5.5-9.5
Total suspended solids (mg/litre)	80	80-200
Barium (as Ba) (mg/litre)	20	-
Cadmium (as Cd) (mg/litre)	0.02	0.02
Chromium III (as Cr) (mg/litre)	2	4
Chromium VI (as Cr) (mg/litre)	0.2	0.2
Iron (as Fe) (mg/litre)	2	4
Nickel (as Ni) (mg/litre)	2	4
Lead (as Pb) (Mg/litre)	0.2	0.3
Copper (as Cu) (mg/litre)	0.1	0.4
Zinc (as Zn) (mg/litre)	0.5	1
Cyanides (as CN) (mg/litre)	0.5	1
Fluorides (as F) (mg/litre)	6	12
Total phosphorus (as P) (mg/litre)		
- into public sewers and surface waters other than lakes	10	10
- into lakes	0.5	0.5

Existing plants discharging into surface waters must satisfy the limits in Table 9D for discharges into public sewers within 3 years and the limits for discharges into surface waters within 9 years. Those discharging into public sewers must satisfy the requirement for such discharge within 3 years.

Singapore

The discharge of industrial effluents (generally referred to as trade effluents) into public sewers or watercourses is governed by a general set of standards stipulated in the Trade Effluent Regulations, 1976. The physical and chemical characteristics of the trade effluent discharged shall not exceed the allowable limits given in Table 9E. The controlled watercourses are defined as those from which water supplied by the Public Utilities Board is obtained, but excluding those from which water is pumped into a main belonging to the Board.

Table 9E: Standards for the discharge of metal finishing effluents (Singapore)

Characteristic	Standards for discharges into:		
	Public sewers	Watercourses	Controlled watercourses
pH	6-9	6-9	6-9
Barium (mg/litre)	10	5	5
Cadmium (mg/litre)	1.0	0.1	0.01
Chromium (III and VI) (mg/litre)	5.0	1	0.05
Iron (mg/litre)	50	20	1
Nickel (mg/litre)	10	1	0.1
Lead (mg/litre)	5	0.1	0.1
Copper (mg/litre)	5	0.1	0.1
Zinc (mg/litre)	10	1	0.5
Cyanide (as CN) (mg/litre)	2	0.1	0.1
Phosphate (as PO_4) (mg/litre)	-	5	2

United Kingdom

No legally enforceable standards exist in the United Kingdom for the discharge of metal finishing effluents, either to surface waters or to sewers; each case is considered on its merits by the appropriate Regional Water Authority and no discharge is permitted without their consent. Any such consent to discharge effluent into a watercourse may be made subject to the fulfillment of certain conditions; contraventions of those conditions are punishable by fines. A consent to discharge effluent into a public sewer may also be made subject to certain conditions; the Authority may, in addition, require the discharger to pay certain charges for the treatment of the effluent.

The Yorkshire Water Authority has given some guidance on the discharge into streams of effluents in which the polluting substances are mainly in solution and often toxic, a group that includes metal finishing wastes. Consent working standards put forward by the Authority for such effluents include the items relevant to metal finishing wastes shown in Table 9F.

Table 9F: Consent working standards for metal finishing wastes
(Yorkshire Water Authority, UK)

Characteristic	Limiting value
Uncomplexed cyanide (mg/litre)	1
Cadmium (mg/litre)	0.2
Copper (mg/litre)	0.5
Lead (mg/litre)	0.5
Chromium (mg/litre)	0.5
Nickel (mg/litre)	0.5
Zinc (mg/litre)	2
Total iron (mg/litre)	5
Suspended solids (mg/litre)	30
pH	6 - 9

For discharges into public sewers, the Yorkshire Water Authority specifies that the pH of all trade effluents must be in the range 5 - 10 and that the concentration of hydrocyanic acid and all compounds that produce hydrocyanic acid on acidification must not exceed 10 mg/litre. The Authority has also made available indicative values of the concentrations of other constituents that it may wish to control; these are shown in Table 9G. Actual values are subject to negotiation between the Authority and the discharger.

Table 9G: Guidelines for the discharge of metal finishing wastes into public sewers (Yorkshire Water Authority, UK)

Characteristic	Indicative limiting value
	(mg/litre)
Suspended solids	500
Total cadmium	2
Total chromium	5
Total lead	5
Total zinc	10
Total copper	5
Total nickel	4

Effluent disposal to land is covered by codes of practice issued by the Department of the Environment. Thus the Code of Practice for Metal Finishing Wastes, published in 1976, states that the concentration of cadmium already present in the land should not be significantly increased by such disposal. Special requirements apply to disposal to landfill sites used for domestic refuse and to agricultural land, unless the wastes are buried deeper than 2 m, as follows:

Type of land	Limiting cadmium concentration in waste
Landfill sites for domestic refuse	10 mg/kg (approx.)
Agricultural land	2.5 mg/kg

With regard to sludges and solids containing cyanide, the Code of Practice for Heat Treatment Cyanide and Related Wastes, also published in 1976, give the guidelines shown in Table 9H.

Table 9H: Guidelines for the disposal of cyanide-containing sludges and solids to land (United Kingdom) (g/m³)

Conditions	Maximum cyanide content of waste	Average cyanide content over the site
Site provides significant containment	1000	10
Underlying strata allow only slow leachate migration	10	1
Underlying strata allow rapid leachate migration	1	-

United States of America

Under the Federal Water Pollution Control Act Amendments of 1972 and the Clean Water Act of 1977, the US Environmental Protection Agency has investigated the electroplating and metal finishing point source categories and has proposed effluent limitation regulations. However, as of January 1983 only pretreatment standards for existing sources (PSES) for the electroplating industry were in effect. A proposal to establish effluent limitation standards for the metal finishing category would have the effect of shifting most electroplaters under the coverage. Under the proposed regulations metal finishing sources would be required to immediately comply with the standards specified for the "best practicable control technology currently available" (BPT). "Best available technology economically achievable" (BAT) standards would be mandatory by 1 July 1984. However, conventional pollutants (oil and grease, total suspended solids and pH) are not covered by BAT and will be subject to a future "best conventional pollutant control technology" (BCT) regulation. New sources will be required to meet new source performance standards (NSPS) and existing and new sources discharging to publicly-owned treatment works will be required to meet pretreatment standards for existing sources (PSES) and new sources (PSNS).

The proposed BPT, BAT, PSES, NSPS and PSNS standards are shown in Table 9I. In no case is a user permitted to augment the use of process waste water or otherwise dilute the waste water as a partial or total substitute for adequate treatment.

Table 9I: Proposed effluent limitations for metal finishing plants (USA) (mg/l)

	BPT		BAT		PSES		NSPS		PSNS	
	Max. for any 1 day	Max. ave. of daily values for 30 consec. days	Max. for any 1 day	Max. ave. of daily values for 30 consec. days	Max. for any 1 day	Max. ave. of daily values for 30 consec. days	Max. for any 1 day	Max. ave. of daily values for 30 consec. days	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
Cadmium	1.29	0.27	1.29	0.27	1.29	0.27	0.064	0.018	0.064	0.018
Chromium	2.87	0.80	2.87	0.80	2.87	0.80	2.87	0.80	2.87	0.80
Copper	3.72	1.09	3.72	1.09	3.72	1.09	3.52	1.09	3.72	1.09
Lead	0.67	0.23	0.67	0.23	0.67	0.23	0.67	0.23	0.67	0.23
Nickel	3.51	1.26	3.51	1.26	3.51	1.26	3.51	1.26	3.51	1.26
Silver	0.44	0.13	0.44	0.13	0.44	0.13	0.44	0.13	0.44	0.13
Zinc	2.64	0.80	2.64	0.80	2.64	0.80	2.64	0.80	2.64	0.80
Cyanide	1.30	0.28	1.30	0.28	1.30	0.28	1.30	0.28	1.30	0.28
Total Toxic Organics	0.58	-	0.58	-	0.58	-	0.58	-	0.58	-
Oil and grease	42	17	-	-	-	-	42	17	-	-
TSS	61	23	-	-	-	-	61	23	-	-
pH	6.0-9.0	-	-	-	-	-	6.0-9.0	-	-	-

3.9.4. References

1. Indian Standards Institution, Tolerance limits for industrial effluents discharged into inland surface waters, electroplating industry, New Delhi IS: 2490, part V (1974).
2. Italy, Law No.319 of 10 May 1976 prescribing rules for the protection of waters against pollution, Gazzetta Ufficiale della Repubblica Italiana, part I, No.141, pp. 4125-4139, 29 May, 1976.
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6. Lancy, L.E., Pollution control in plating operations, In: Lund, H.E., ed., Industrial pollution control handbook, New York, McGraw-Hill, pp. 12-1 - 12-16 (1971).
7. United Kingdom, Heat-treatment cyanide wastes, London, Department of the Environment, HMSO, Waste Management Paper No.8 (1976).
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9. United Kingdom, Disposal of sewage sludge to land, London, Department of the Environment, Technical Committee, Report No.20 (1981).
10. United States Of America, Electroplating point source category, Title 40, part 413, Code of Federal Regulations, Washington DC, US Government Printing Office, pp. 198-206 (1977).
11. United States Of America, Electroplating and metal finishing point source categories, effluent limitation guidelines pretreatment standards and performance standards, Federal Register, vol. 47, No.167, (31 August 1982).
12. Canada, Metal finishing liquid effluent guidelines, Ottawa, Department of the Environment, Report EPS 1-WP-77-5 (1977).

3.10. PETROCHEMICALS

The petrochemical industry produces, from a petroleum feedstock, a wide variety of organic chemicals ranging from simple hydrocarbons to complex polymers. However, the more complex products will not be considered here.

3.10.1. Outline of process

The petroleum feedstock (usually light naphtha) is subjected to medium-temperature steam cracking in a tubular reactor. After cracking, the gas mixture is quickly cooled to avoid undesirable polymerization and decomposition. The main reaction products are ethylene and its higher homologues, together with aromatics (benzene, toluene and xylenes), and a heavy pyrolysis fuel oil. These primary petrochemicals can then undergo a large number of secondary processes, such as hydrogenation, alkylation, etc., to produce compounds such as cyclohexane, styrene, dodecylbenzene, ethylene oxide, acrylonitrile and vinyl chloride.

3.10.2. Sources of pollution

Water is used for quenching the reaction products from steam cracking and gives rise to a highly polluted effluent containing both dissolved and suspended hydrocarbons. The former can be removed by air stripping followed by passage of the stripping gas through a combustion furnace, the latter by settling.

The various secondary petrochemical processes produce a variety of effluents. For example, the production of ethylene oxide by the use of a silver catalyst gives rise to wastewaters containing sodium bicarbonate and organics. The organics are treated biologically, as are the wastewaters from the manufacture of acetaldehyde from ethylene with a copper or palladium catalyst. Where the wastewaters contain organochlorine compounds toxic to bacteria, saponification with alkali prior to biological treatment is necessary. Chlorinated hydrocarbons can also be removed by air stripping, while hydrocarbons can be stripped out with nitrogen and removed by activated carbon. Toxic nitriles, produced in the manufacture of acrylonitrile by the Sohio process, can be removed by saponification under pressure.

3.10.3. Discharge standards

United States of America

Under the Clean Air Act, the US Environmental Protection Agency has promulgated National Emission Standards for Hazardous Air Pollutants (NESHAPS). Table 10A lists the emission standards for vinyl chloride from a number of specified manufacturing processes.

Table 10A: Vinyl chloride emission standards (USA)

Sources	Emission standard	Sampling or monitoring requirement
Ethylene dichloride manufacture	1) Ethylene dichloride purification: 10ppm* 2) Oxychlorination reactor: 0.2 g/kg (0.0002 lb/lb) of the 100% ethylene dichloride product	Source test Continuous monitor Source test Continuous monitor
Vinyl chloride manufacture	10 ppm*	Source test Continuous monitor
Polyvinyl chloride manufacture		
Reactor; stripper; mixing; weighing and holding containers; monomer recovery system	10 ppm*	Source test Continuous monitor
Reactor opening loss	0.02 g vinyl chloride/kg (0.00002 lb vinyl chloride/lb)	Source test Continuous monitor
Reactor manual vent	No emissions	
Sources following stripper	For each calendar day: 1) Using stripping technology - 2000 ppm for polyvinyl chloride dispersion resins (excluding latex) 400 ppm each for other polyvinyl chloride resins (including latex)	Source test

Ethylene dichloride, vinyl chloride and/or polyvinyl chloride manufacture	2) Other than stripping technology - 2 g/kg (0.002 lb/lb) product for dispersion polyvinyl chloride resins (excluding latex) 0.4 g/kg (0.0004 lb/lb) product for other polyvinyl chloride resins (including latex)	Source test
Relief valve discharge	No discharge	Equipment
Loading and unloading lines	0.0038 m ³ after each loading or unloading, or 10 ppm when contained by a control system	Source test Continuous monitor
Slip gauges	10 ppm from the required control system	Source test Continuous monitor
Pump; compressor and agitator seal	10 ppm from the required control system with seals	Source test Continuous monitor
Leakage from relief valves	Rupture disk must be installed	Equipment
Manual venting of gases	10 ppm from a required control system	Source test Continuous monitor
Opening of equipment	10 ppm from a required control system*	Source test Continuous monitor
Samples (at least 10 percent by weight vinyl chloride)	Returned to system	
Leak detection and elimination	Implementation of an approved program	Approved testing program
Inprocess wastewater	10 ppm before discharge	Source test Continuous monitor
	* Before opening any equipment for any reason, the quantity of vinyl chloride is to be reduced so that the equipment contains no more than 2.0 percent by volume vinyl chloride or 0.0950 m³ (25 gal) of vinyl chloride, whichever is larger, at standard temperature and pressure.	

Under the Federal Water Pollution Control Act Amendments of 1972, the US Environmental Protection Agency has issued detailed effluent limitations for wastewaters from petrochemical plants. These form the petrochemical subcategory of the petroleum refining point source category. Effluent limitations are given both for existing and for new petrochemical plants, and both for the "best practicable control technology currently available" (BPT) and for the "best available technology economically achievable" (BAT).

The basic effluent limitations for existing petrochemical plants are shown in Table 10B. Values from this table must be adjusted by factors derived from the size of a plant and the particular process involved to give the actual effluent limitation for a particular plant. The actual limitation is related to the basic limitation as follows: actual effluent limitation = basic effluent limitation x size factor x process factor.

Size factors (which depend on the refinery feedstock flow-rate) are given in Table 10C. Process factors are given in Table 10D, however, before it is possible to select the process factor applicable to a plant from this table, it is necessary to work out the process configuration for that plant by means of weighting factors for the various processes undertaken at the plant. The weighting factors are given in Table 10E.

The procedure may be explained as follows: Each petrochemical plant will contain a number of different processes. For each process, the ratio of capacity to throughput is multiplied by the weighting factor in Table 10E to give the corresponding process configuration for that process. Process configurations for the various processes at the plant are then summed to give the process configuration for the refinery.

Table 10B: Effluent limitations for the petrochemicals subcategory
(existing plant) (USA) (kg/1000 m³ of feedstock)

Effluent characteristic	Max. for any 1 day		Max. ave. of daily values for 30 consec. days	
	BPT	BAT	BPT	BAT
BOD ₅	34.6	21.8	18.4	11.6
Total suspended solids	23.4	14.9	14.8	9.5
COD	210	133	109	69
Oil and grease	11.1	6.6	5.9	3.5
Phenolic compounds	0.25	0.158	0.120	0.077
Ammonia (as N)	23.4	23.4	10.6	10.7
Sulfide	0.22	0.140	0.099	0.063
Total chromium	0.52	0.32	0.30	0.19
Chromium VI	0.046	0.025	0.020	0.012
pH	6.0-9.0	6.0-9.0	-	-

Table 10C: Size factors for the petrochemicals subcategory (USA)

Feedstock flow-rate (1000 bbl per stream day)	Size factor
24.9	0.73
25.0 - 49.9	0.76
50.0 - 74.9	0.83
75.0 - 99.9	0.91
100.0 - 124.9	0.99
125.0 - 149.9	1.08
150.0 or greater	1.13

Table 10D: Process factors for the petrochemicals subcategory (USA)

Process configuration	Process factor
4.49	0.73
4.5 - 5.49	0.80
5.5 - 5.99	0.91
6.0 - 6.49	0.99
6.5 - 6.99	1.08
7.0 - 7.49	1.17
7.5 - 7.99	1.28
8.0 - 8.49	1.39
8.5 - 8.99	1.51
9.0 - 9.49	1.65
9.5 of greater	1.72

Table 10E: Values of weighting factor for calculation of process configuration (USA)

Process category	Process included	Weighting factor
Crude	Atmospheric crude distillation	1
	Vacuum crude distillation	
	Desalting	
Crackling and coking	Fluidized catalytic cracking	6
	Visbreaking	
	Thermal cracking	
	Moving-bed catalytic cracking	
	Hydrocracking	
	Fluidized coking	
	Delayed coking	
Lube	-	13
Asphalt	Asphalt production	12
	Asphalt oxidation	
	Asphalt emulsifying	

Where waste waters are discharged into a publicly-owned treatment plant, the following pretreatment standards apply:

	Maximum for any 1 day (mg/litre)
Ammonia (as N)	100
Oil and grease	100

For new petrochemical plants, the limitations given in Table 10F apply. These must be multiplied by the size factors and the process factors given in Tables 10C and 10D respectively.

Table 10F: Effluent limitations for the petrochemicals subcategory
 (new plants) (USA) (kg/1000 m³ of feedstock)

Effluent characteristic	Maximum for any 1 day	Max. ave. of daily values for 30 consec. days
BOD ₅	21.8	11.6
Total suspended solids	14.9	9.5
COD	133	69
Oil and grease	6.6	3.5
Phenolic compounds	0.158	0.077
Ammonia (as N)	23.4	10.7
Sulfide	0.140	0.063
Total chromium	0.32	0.19
Chromium	0.025	0.012
pH	6.0-9.0	-

3.10.4. References

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4. United States of America, National emission standards for hazardous air pollutant, Washington DC, US Environmental Protection Agency, EPA/340/1-82-006 (August 1982).

3.11. PETROLEUM REFINING

Crude oil, which consists essentially of a mixture of liquid hydrocarbons, is converted by refining into more than 2500 different products, including liquefied petroleum gas (LPG), gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils and feedstocks for the petrochemical industry. At the same time, impurities, and especially sulfur, are removed.

3.11.1. Outline of process

The first stage in the refining of petroleum is the storage of the crude oil. The crude is then separated by distillation into hydrocarbon mixtures of various boiling ranges, which may be designated light hydrocarbons, middle and heavy distillates, and residual hydrocarbons. These mixtures are treated in various ways in order to obtain refined products having the desired characteristics, and then stored. The process can therefore be divided into the following stages:

- crude and refined product
- crude separation
- light hydrocarbon processing
- middle and heavy distillate processing
- residual hydrocarbon processing

3.11.2. Sources of pollution

Many petroleum refining operations are carried out in closed systems and therefore do not give rise to any emissions; those that do are indicated below. In addition, fugitive emissions from pump seals, valves, relief vents and leaks may be important.

Storage - Both crude oil and refined product are stored in cone-roof or floating-roof tanks. Hydrocarbon vapours may be emitted as a result of tank breathing due to temperature changes, or to evaporation and displacement during filling.

Crude separation - The operations involved in crude separation are shown in Table 11A.

Light hydrocarbon processing - After removal of sulfur and nitrogen compounds, the octane rating of hydrocarbons can be upgraded by the methods shown in Table 11B.

Middle and heavy distillate processing - This performs a number of functions as shown in Table 11C.

Residual hydrocarbon processing - This is used to upgrade the value of the residuum left after the atmospheric or vacuum distillation of crude, as shown in Table 11D.

Table 11A: Crude separation

Operation	Purpose and method	Emissions
Desalting	Removal of inorganic salts by mixing with water followed by separation	Desalter water
Atmospheric distillation	Separation of crude into fractions	-
Hydrogen sulfite removal	Treatment of hydrocarbon gases from crude distillation with amine solution	Spent amine solutions
Sulfur recovery	Recovery of sulfur from amine solution	Sulfur dioxide
Gas processing	Production of pure products from gases from crude distillation	Sulfidic spent caustic
Vacuum distillation	Separation of residue from atmospheric distillation	Contaminated condensate

Table 11B: Light hydrocarbon processing

Operation	Purpose and method	Emissions
Naphtha	Removal of sulfur and nitrogen compounds	Carbon monoxide from catalyst regeneration
Catalytic reforming	Conversion of naphthas into high octane reformates in fixed-bed catalytic reactor	Carbon monoxide from catalyst regeneration
Isomerization	Conversion of normal compounds into isoparaffins	Aqueous wastes from neutralization vessel
Alkylation	Reaction of olefin and isoparaffin to produce high octane alkylate, using sulfuric or hydrofluoric acid	Fluoride, when hydrofluoric acid used as catalyst
Polymerization	As for alkylation, but two olefin gases used as feed and phosphoric acid as catalyst	Washings containing phosphoric acid

Table 11C: Middle and heavy distillate processing

Operation	Purpose and method	Emissions
Chemical sweetening	Removal of odoriferous sulfur compounds by caustic scrubbing and water washing	Spent caustics
Hydrodesulfurization	Production of high-quality, low-sulfur products in fixed-bed catalytic reactor	Carbon monoxide from catalyst regeneration
Fluidized-bed catalytic cracking	Conversion of heavy gas oils into lighter products by means of fluidized zeolitic catalyst	Spent catalyst and catalyst fines, from catalyst regeneration
Moving-bed catalytic cracking	As above, but moving-bed catalytic reactor	Spent catalyst and carbon monoxide from catalyst regeneration
Hydrocracking	As above, but reaction carried out in presence of high-pressure hydrogen	Carbon monoxide from catalyst regeneration
Lube oil processing	Improvement of properties of lubricating oil base stocks by solvent extraction or sulfuric acid treatment	Solvent-contaminated liquid effluents, or acid sludges and waste clay from catalyst regeneration
Lube hydrotreating	As above, but carried out in fixed-bed reactor in presence of hydrogen	Carbon monoxide from catalyst regeneration

Table 11D: Residual hydrocarbon processing

Operation	Purpose and method	Emissions
Deasphalting	Removal of asphaltic materials by solvent extraction; solvent recovered by evaporation	Contaminated condensate
Asphalt blowing	Oxidation of heavy residual oils by blowing air through heated oil	Highly odoriferous vent gases
Visbreaking	Thermal cracking of residual oils to reduce their viscosity	Sour water waste stream from fractionator
Coking	Vapor/liquid mixture from heater passed to coke drum	Particulates from coke dust on equipment; odours from wash water on storage if equipment is washed; contaminated cooling water from drum
Catalytic hydro-desulfurization	Reduction of concentrations of sulfur nitrogen and metals in residual oils	Carbon monoxide from catalyst regeneration

3.11.3. Discharge standards

Canada

Wastewaters from new petroleum refineries are governed by Liquid Effluent Regulations of 30 October 1973, made under the Fisheries Act, as amended in 1970. The Regulations specify the "authorized deposits" of "deleterious substances", defined as oil and grease, phenols, sulfides, ammonia nitrogen, and total suspended solids, as shown in Table 11E.

Table 11E: Authorized deposits of deleterious substances(Canada) (in lb/1000 bbl of crude oil)

Substance	Monthly amount	1-day amount	Max. daily amount
Oil and grease	3.0	5.5	7.5
Phenols	0.3	0.55	0.75
Sulfides	0.1	0.3	0.5
Ammonia nitrogen	3.6	5.7	7.2
Total suspended matter	7.2	12.0	15.0

Special provisions apply when storm waters are being discharged, as shown in Table 11F.

Table 11F: Special provisions applicable when storm waters are being discharged (Canada)

Substance	Additional authorized deposit	Limit of deposits authorized
	(1b/10 000 Canadian gallons of storm water)	(1b/month per 1000 bbl of crude oil per day)
Oil and grease	1.0	25.0
Phenols	0.1	2.5
Total suspended matter	3.0	75.0

In addition to the Regulations, the Federal Government has also published guidelines for petroleum refineries. Thus, the "Guidelines respecting acute toxicity of liquid effluents from petroleum refineries" state that refinery liquid effluent and once-through cooling water is not acceptable if more than 50% of fish (Salmo gairdneri) die in a 96-hour flow-through test procedure.

With regard to the quality of liquid effluents from existing refineries, the figures shown in Table 11G are given in the guidelines.

Table 11G: Quality of liquid effluents from existing petroleum refineries (Canada)
(in lb/1000 bbl of crude oil)

Substance	Monthly amount	1-day amount	Max. daily amount
Oil and grease	6.0	11.0	15.0
Phenols	0.6	1.1	1.5
Sulfides	0.2	0.6	1.0
Ammonia nitrogen	5.0	8.0	10.0
Total suspended matter	14.4	24.0	30.0

There are also special guidelines for the conditions when storm water is being discharged, as shown in Table 11H.

Table 11H: Special guidelines applicable when storm water is being discharged (Canada)

Substance	Additional deposit (lb/10 000 Canadian gallons of storm water)	Limit of deposit (lb/month per 1000 bbl of crude per day)	
		Altered or expanded refineries	Existing refineries
Oil and grease	1.0	25.0	50.0
Phenols	0.1	2.5	5.0
Total	3.0	75.0	150.0

Finally, the guidelines on the acute toxicity of liquid effluents from existing petroleum refineries make the same recommendations as those for new refineries.

France

Regulations on liquid effluents from new refineries specify that treated effluents must conform to the requirements given in Table lII. Various types of refineries are distinguished in the French regulations. Type A refineries are skimming plants with distillation, reforming and desulfurization. The maximum volume of discharged water (excluding rain and ballast water) per tonne of crude oil processed is respectively 0.4 cubic metres. Type B refineries are Type A refineries plus catalytic cracking, while Type C refineries also have steam cracking and/or lube oil. The maximum volume of discharged water (excluding rain and ballast water) per tonne of crude oil processed is respectively 0.8 and 1.2 cubic metres.

Table lII: Requirements applicable on a daily representative basis to treated liquid effluents from new refineries (France)

Item	Type A refineries	Type B and Type C refineries
Temperature (°C)	30	30
pH	5.5 - 8.5	5.5 - 8.5
BOD ₅ (mg/litre)	30	40
COD (mg/litre)	120	150
Suspended matter (mg/litre)	30	30
Hydrocarbons (by hexane extraction) (mg/litre)	5	5
Hydrocarbons (infrared) (mg/litre)	20	20
Phenols (mg/litre)	0.5	1
Lead (mg/litre)	0.1	0.1
Hexavalent chromium (mg/litre)	0.05	0.05

Germany (Federal Republic)

Guidelines for waste waters from petroleum refineries have been published by the Länderarbeitsgemeinschaft Wasser, and are shown in Table 11J.

Table 11J: Guidelines for wastewaters from petroleum refineries (FRG)

Item	Recommended value after:		
	Mechanical treatment	Chemical treatment	Biological treatment
Settleable solids (ml/litre)	0.3	0.3	0.3
Suspended solids	Nil	Nil	Nil
Extractable matter (in diethylether) (ml/litre)	20	10	5
pH	-	6.0 - 9.0	-
Oil sheen	-	-	None
BOD ₅ (ml/litre)	-	-	30
Sulfides	-	1	Not detectable
Phenols (volatile) (mg/litre)	-	-	0.5

United States of America

Under the Clean Air Act amendments, the US Environmental Protection Agency was empowered to adopt national emission standards for new or modified stationary sources making a significant contribution to air pollution. The standards for petroleum refineries are listed in Table 11K.

Table 11K: New source performance standards for petroleum refineries (USA)

Source	Pollutant	Emission level	Monitoring requirement
Catalytic cracker	Particulate	1.0 lb/1000 lb (1.0 kg/100 kg)	No requirement
(with incinerater or waste heat boiler)		Additional 0.10 lb/10 ⁶ Btu(43.0 g/MJ)	No requirement
	Opacity	30%; 6 min. exemption	Continuous
	CO	0.05%	Continuous
Fuel gas combustion	SO ₂	0.10 gr H ₂ S/dscf	Continuous
Claus sulfur recovery plants ➤20 LTD/day (as of 10/4/76)	SO ₂	0.025% with oxidation or reduction and incineration; 0.030% with reduction only	Continuous
Storage tanks ^(a) 65,000 gal. capacity (246,052 litres) as at 6/11/73 and 40,000 gal. capacity (151,412 litres) as of 3/8/74	Volatile organic compounds (VOC)	Vapor pressure 1.5-11.1 psia (78-570 mm Hg), equip. with floating roof, vapor recovery system or equivalent	No requirement
		Vapor pressure ➤11.1 psia (570 mm Hg), equip. with vapor recovery system or equivalent	No requirement
Storage tanks ^(b) 740,000 gal. capacity (151,416 litres)	Volatile organic compounds (VOC)	Vapor pressure 1.5-11.1 psia (10.3-76.6 k Pa), equip. with floating roof or fixed roof with internal floating cover (both must meet specifications), or vapor recovery and disposal system reducing emissions at least 95%	No requirement

Type of liquid
period of storage,
and maximum vapor
pressure

- (b) constructed after May 18 1978

Under the Federal Water Pollution Control Act Amendments of 1972 and the Clean Water Act of 1977, the US Environmental Protection Agency has also issued detailed effluent limitations guidelines and standards for wastewaters from both existing and new petroleum refineries. These cover what are called the topping, cracking, petrochemical lube, and integrated subcategories. The limitations are given for the "best practicable control technology currently available" (BPT) and for the "best available technology economically achievable" (BAT).

Because of the complexity of the standards, reference should be made to Part 419 of Title 40 of the Code of Federal Regulations for full details; the limitations for the integrated subcategory will alone be considered here. This subcategory includes all facilities producing petroleum products by the use of topping, cracking, lube oil manufacturing processes and petrochemical operations. The effluent limitations for existing refineries in this subcategory are shown in Table 11L. Values from this table must be adjusted by factors derived from the size of a plant and the particular process involved to give the actual effluent limitation for a particular plant. The actual limitation is related to the basic limitation as follows:

Actual effluent limitation = basic effluent limitation x size factor x process factor.

Table 11L: Effluent limitations for the integrated subcategory
(existing refineries) (USA) (kg/1000 m³ of feedstock)

Effluent characteristic	Max. for any one day		Max. ave. of daily values for 30 consec. days	
	BPT	BAT	BPT	BAT
BOD ₅	54.4	-	28.9	-
Total suspended solids	37.3	-	23.7	-
COD	388.0	388.0	198.0	198.0
Oil and grease	17.1	-	9.1	-
Phenolic compounds	0.40	0.40	0.192	0.192
Ammonia (as nitrogen)	23.4	23.4	10.6	10.6
Sulfide	0.35	0.35	0.158	0.158
Total chromium	0.82	0.068	0.48	0.032
Hexavalent chromium	0.068	0.068	0.032	0.032
pH	6.0-9.0	-	6.0-9.0	-

Size factors (which depend on the refinery feedstock flow-rate) are given in Table 11M. Process factors are given in Table 11N; however, before it is possible to select the process factor applicable to a plant from this table it is necessary to work out the process configuration for that plant by means of weighting factors for the various processes undertaken at the plant. The weighting factors are given in Table 11O.

Table 11M: Size factors for the integrated subcategory (USA)

Feedstock flow-rate (1000 bbl per stream day)	Size factor
less than 124.9	0.73
125.0 - 149.9	0.76
150.0 - 174.9	0.83
175.0 - 199.9	0.91
200.0 - 224.9	0.99
225 or greater	1.04

Table 11N: Process factors for the integrated subcategory (USA)

Process configuration	Process factor
6.49 or less	0.75
6.5 - 7.49	0.82
7.5 - 7.99	0.92
8.0 - 8.49	1.00
8.5 - 8.99	1.10
9.0 - 9.49	1.20
9.5 - 9.99	1.30
10.0 - 10.49	1.42
10.5 - 10.99	1.54
11.0 - 11.49	1.68
11.5 - 11.99	1.83
12.0 - 12.49	1.99
12.5 - 12.99	2.17
13.0 or greater	2.26

Table 110: Values of weighting factor for calculation of process configuration (USA)

Process category	Processes included	Weighting factor
Crude	Atmospheric crude distillation	1
	Vacuum crude distillation	
	Desalting	
Cracking and coking	Fluidized catalytic cracking	6
	Visbreaking	
	Thermal cracking	
	Moving-bed catalytic cracking	
	Hydrocracking	
	Fluidized coking	
	Delayed coking	
Lube	-	13
Asphalt	Asphalt production	12
	Asphalt oxidation	
	Asphalt emulsifying	

The procedure may be explained as follows: Each refinery will contain a number of different processes. For each process, the ratio of capacity to throughput is multiplied by the weighting factor in Table 110 to give the corresponding process configuration for that process. Process configurations for the various plants are then summed to give the process configuration for the refinery.

There are additional allowances for storm runoff flow and ballast water flow. Once-through cooling water may be discharged with a total organic carbon concentration not exceeding 5 mg/litre.

Where wastewaters are discharged into a publicly-owned treatment plant, the following standard applies:

<u>Pollutant</u>	<u>Maximum for any 1 day</u> <u>(mg/litre)</u>
Ammonia (as nitrogen)	100
Oil and grease	100

For new refineries, the limitations given in Table 11P apply. These must be multiplied by the size factors and process factors given in Tables 11M and 11N respectively. There are additional allowances for storm runoff and ballast water flow. As for existing refineries, once-through cooling water may be discharged with a total organic carbon concentration not exceeding 5 mg/litre.

Table 11P: Effluent limitations for the integrated subcategory (new refineries) (USA)
(kg/1000 m³ of feedstock)

<u>Effluent characteristic</u>	<u>Maximum for any one day</u>	<u>Max. ave. of daily values for 30 consec. days</u>
BOD ₅	41.6	22.1
Total suspended solids	28.1	17.9
COD	295.0	152.0
Oil and grease	12.6	6.7
Phenolic compounds	0.30	0.14
Ammonia (as nitrogen)	23.4	10.7
Sulfide	0.26	0.12
Total chromium	0.64	0.37
Hexavalent chromium	0.052	0.024
pH	6.0 - 9.0	6.0 - 9.0

3.11.4. References

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3.12. PULP AND PAPER

In the pulp and paper industry a number of different processes are used to disintegrate suitable prepared wood so as to free the cellulose fibres from the lignin which binds them together. The processes may be either chemical and/or mechanical. The pulp product is then dewatered after bleaching (where necessary) in order to obtain paper.

3.12.1. Outline of process

The wood is first prepared by washing and debarking. Unless mechanical pulping (groundwood process) is to be used, the wood is converted into small chips of uniform size to facilitate chemical digestion. This may be carried out by one of three main chemical processes:

Kraft pulping, with a mixture of sodium hydroxide and sodium sulfite;
sulfite pulping, with an acidic liquor containing a bisulfite;
neutral sulfite semichemical (NSSC) pulping with a neutral mixture of sodium sulfite and sodium carbonate followed by mechanical disintegration.

Pulping may be followed by bleaching with an oxidizing agent and finally, in papermaking, the fibre slurry is dewatered to form a wet sheet and then smoothed and dried.

3.12.2. Sources of pollution

Wood preparation gives rise both to wastewaters containing suspended and dissolved solids, and to solid wastes.

Mechanical pulping produces only relatively small amounts of pollutants; however, all three chemical pulping processes produce highly polluted wastewaters. The pollutants include suspended solids and oxygen-consuming substances. The suspended solids may be removed by filtration, sedimentation and flotation while the oxygen-consuming substances can be removed by biological treatment methods such as oxidation ponds, trickling filters and the activated-sludge process. Pulp-mill wastewaters are also discoloured by dissolved lignin compounds and a number of colour-removal processes are currently under development.

Papermaking effluents contain both suspended and dissolved solids while the bleaching process produces wastewaters containing oxygen-consuming substances.

Odoriferous materials (i.e. reduced sulfur compounds) may be produced in kraft pulping as a result of the reaction between small amounts of sulfide and lignin. These sulfur compounds can also be produced in the treatment of the spent cooking liquor (black liquor). The kraft process also gives rise to suspended particulate matter emissions.

Sulfite pulping does not produce odour problems as the main gaseous pollutant is sulfur dioxide. The Neutral Sulfite Semi-Chemical (NSSC) process gives rise to odoriferous gases and to sulfur dioxide.

3.12.3. Discharge standards

Australia (Tasmania)

The Tasmanian Environment Protection (Water Pollution) Regulations 1974, made under the Environment Protection Act 1973, as amended in 1977, contain the discharge standards shown in Table 12A.

Table 12A: Discharge standards for pulp and paper mills (Tasmania)

Type of process	BOD (kg/tonne of air dry product)	Non-filtrable residue (mg/litre)	Mercury (mg/litre)
All types	-	200	0.005
Full chemical pulping	25	-	-
Cold caustic semi- chemical pulping	45	-	-
Other semi-chemical pulping	90	-	-
Full chemical pulp bleaching	15	-	-
Semi-chemical pulp bleaching	55	-	-
Paper and board manufacture	10	-	-
Hardboard manufacture	90	-	-

In addition, the following standards are laid down for woodchip mills:

BOD	170 g/tonne of product at 50% moisture content
Non-filtrable residue	240 g/tonne of product at 50% moisture content

Under the Environment Protection Act, failure to comply with the standards laid down in the Regulations is an offence punishable by a fine on conviction.

Canada

The Federal Government has made regulations governing wastewaters discharged by pulp and paper mills. These regulations were made pursuant to the Fisheries Act, as amended in 1970, which empowered the Government to regulate fisheries and relevant aspects of pollution control. The provinces also have the power to establish their own standards, provided that they are at least as stringent as those established by the Federal Government. The federal standards can also be made more stringent, if this is required by the condition of the receiving waters.

The permitted amounts of oxygen-consuming substances are shown in Table 12B and those of suspended solids in Table 12C. The regulations also specify that at least 80% of a given species of fish must survive for 96 hours in a mixture comprising 65% of treated wastewaters and 35% of water.

With regard to air pollution the Federal government has published National Emission Guidelines indicating the quantities and concentrations above which particulate matter, total reduced sulfur compound and sulfur dioxide should not be emitted from new sulfate (kraft) and new sulfite pulping plants.

Table 12B: Permitted amounts of oxygen-consuming substances in chemical pulp mill wastewater (Canada) (in lb BOD/air dry short ton of product)

Process	Existing mill	New altered or expanded mill
Sulfite pulping:		
Yield-55% or less	255	170
Yield-greater than 55% but less than 65%	170	115
Yield-65% or more	150	75
Sulfite bleaching (market pulp)	35	35
Kraft pulping	64	33
Kraft bleaching	27	27
Neutral sulfite semi-chemical pulping	80	60

Nb BOD values shown for kraft pulping and bleaching are those permitted in discharges from kraft mills before the waste waters have been passed through a toxicity-reduction system.

Table 12C: Permitted amounts of total suspended solids in pulp and paper mill wastewaters (Canada) (in lb/ton (a))

Process	Existing chemical mill	New, expanded or altered chemical mill	Existing mechanical mill	New, expanded or altered mechanical mill
1. Wood rewashing	5	5	5	5
2. Debarking (hydraulic process)	5	5	5	5
3. Debarking (wet drum process)	10	8	10	8
4. Pulping	7	5	13	10
5. Bleaching	6	4	2	2
6. Pulp sheet formation	2	1	5	4
7. Integrated, single-product papermaking	3	2	5	4
8. Integrated, specialty single-product papermaking	6	4	10	8
9. Tissue papermaking	15	10	20	15
10. Fine and specialty multi-product papermaking	25	20	25	20
11. Cylinder paper or paperboard manufacture	15	12	15	12
12. Neutral sulfite semi-chemical corrugating medium	7	7	-	-

(a) "ton" is defined as follows:

- (i) for items 1-3, as an oven-dry ton of wood processed without the bark;
- (ii) for items 4-6, as an air-dry ton of product;
- (iii) for items 7-12, as a ton of product as produced.

France

The control of wastewaters from existing chemical and semi-chemical pulp mills is based on a July 1972 agreement between the Minister for the Environment and the Chairman of the French Confederation of Paper, Board and Cellulose Industries.

The agreement established a programme for the reduction of pollution, to be carried out in the following stages:

- reduction of amount of suspended solids;
- reduction of amount of oxygen-consuming substances;
- elimination of sludges and solid wastes;
- colour reduction;
- elimination or utilization of spent liquor.

The maximum permitted amounts of suspended solids and oxygen-consuming substances in the wastewaters are shown in Table 12D. Compliance with these limits was to be achieved by certain dates, depending on the size of the mill concerned and its "geographical priority", the latter reflecting the importance of the area in which the mill is situated, from the point of view of water supplies.

There are no regulations concerned specifically with air pollution from the pulp and paper industry.

Table 12D: Maximum permitted amounts of suspended solids and oxygen-consuming substances in wastewaters from chemical pulp mills (France) (kg/tonne)

Process	Stage 1	Stage 2	
	Suspended solids	BOD	Suspended solids
Kraft pulping:			
Unbleached	2.5	5	10
Bleached	10	9	20
Sulfite pulping:			
With elimination or utilization of spent liquor	12.5	45	50
Without elimination or utilization of spent liquor	15	80	85
Neutral sulfite semi-chemical pulping:			
Capacity greater than 150 tonnes/day	5	8	5
Capacity less than 150 tonnes/day	13	60	60

Germany (Federal Republic)

No federal or Land regulations exist setting discharge standards specifically for wastewaters from the pulp and paper industry. However, an expert group established by the Länder (the Länderarbeitsgemeinschaft Wasser) has drawn up standards for treated wastewaters. These standards depend on the type of treatment and the raw materials used (see Table 12E). Land permits to discharge wastewaters are based on these standards.

No federal or Land atmospheric discharge standards exist for the pulp and paper industry. However, as kraft pulping is prohibited, air pollution from the pulp and paper industry is said to be of little importance.

Japan

Under the 1971 Act on pollution control in specified factories, certain minimum standards applicable to the country as a whole were laid down for wastewaters from the pulp and paper industry (see Table 12F). Local authorities were also empowered to specify more stringent standards.

The only specific legislation dealing with air pollution from the pulp and paper mills relates to emissions from boilers and calcining furnaces. The relevant general legislation is the Offensive Odour Control Act of 1 June 1971. This Act is concerned with "offensive odour substances", namely methylmercaptan, hydrogen sulfide, dimethyl sulfide, and similar compounds. The Act lays down that the Governor of the Prefecture is empowered to designate areas where such substances are to be controlled, and requires him to establish control standards for each individual substance.

Sweden

Swedish legislation on water pollution control contains no specific discharge standards for the pulp and paper industry. However under the 1969 Environment Protection Act no pulp or paper mill may be constructed or altered unless a permit to that effect has been granted by the National Franchise Board for Environmental Protection. The Board is guided in reaching a decision to issue a permit by the figures shown in Table 12G. These are indicative limits only, as more stringent requirements can be imposed when necessary.

Guidelines also exist for discharges to the atmosphere from pulp and paper mills (see Table 12H). A requirement of the legislation is that electrostatic precipitators following new recovery furnaces should be constructed with at least two independent sections. The maximum permitted concentration of suspended particulate matter with one section out of operation is 500 mg/m³ of dry gas at STP.

Table 12E: Standards for treated wastewaters from the pulp and paper industry (FRG)

Type of treatment and wastewater characteristics	Type of raw materials used					
	Cellulose	Cellulose and pulp	Cellulose and/or wood pulp with mineral dyes	Cellulose and/or wood pulp with added waste paper	Waste paper only, especially mixed grades	Rags, semi-cellulose straw, etc.
<u>Mechanical</u>						
Insoluble matter (mg/litre)	30	40	40	50	100	100
pH	5.5-9.0	5.5-9.0	5.5-9.0	5.5-9.0	5.5-9.0	5.5-9.0
Bleaching agent	Not detectable	Not detectable	Not detectable	Not detectable	Not detectable	Not detectable
<u>Chemical</u>						
Settleable matter (a) (ml/litre)	0.3	0.3	0.3	0.3	0.3	0.5
Insoluble matter (mg/litre)	20	25	30	40	50	100
pH	5.5-9.0	5.5-9.0	5.5-9.0	5.5-9.0	5.5-9.0	5.5-9.0
COD (mg/litre) (b)	150	300	400	400	400	-
BOD ₅ (mg/litre)	50	200	200	200	200	300
Bleaching agent	Not detectable	Not detectable	Not detectable	Not detectable	Not detectable	Not detectable
<u>Biological</u>						
Settleable matter (ml/litre)	0.3	0.3	0.3	0.3	0.3	0.3
Insoluble matter (mg/litre)	20	20	20	20	30	30
COD (b) (mg/litre)	100	100	150	150	150	200
BOD ₅ (mg/litre)	25	25	25	25	40	30

Table 12F: Emission standards for the pulp and paper industry (Japan) (mg/litre)

Characteristic	Limitation
BOD	120
COD	120
Suspended solids	150

Table 12G: Guidelines for the emission of wastewaters from pulp and paper mills (Sweden) (kg/tonne of pulp)

Characteristic	Mechanical pulping	Sulfate pulping	Sulfite pulping	Semi-chemical pulping	Fibre building board
BOD ₇ from:					
Debarking	1-3	1-3	1-3	1	1
Washing	-	5	3-7	10-15	-
Grinding	15	-	-	-	10-20
Condensate	-	2-3	4-10	5	-
Bleaching	2-15	8-9	10-13	2-15	-
Suspended solids	2-5	2-5	2-5	2-5	2-5

Table 12H: Guidelines for the emission of atmospheric pollutants from pulp and paper mills (expressed as the monthly arithmetic mean of the total emissions during the period of operation (Sweden))

Pollutant	Source	Guidelines for:	
		New mills	Existing mills
Particulate matter (mg/m ³ of dry gas at STP)	Kraft pulping:		
	Recovery furnace	250	500
	Lime kilns	250	250
	Bark boilers	500*	500*
		max 30 kg/h max 30 kg/h	
		*Corrected to an excess of air equivalent to 10% CO ₂ -concentration	
Sulfur dioxide (kg tonne)	Sulfite pulping:		
	Recovery furnace	250	500
	Sulfite pulping:		
	All units except fuel burning	10	20
Odoriferous substances	Kraft pulping	2-5	5
	Kraft pulping:		
	Digester, evaporators	Dilution factor: 10 000	
		Hydrogen sulfide 10 mg/m ³ of dry gas at STP for 95% of the time for new mills and for 90% of the time for existing mills	
	Lime kilns	Hydrogen sulfide 50 mg/m ³ of dry gas at STP for 90% of the time	

United Kingdom

Each discharge of pulp and paper mill effluents is considered on its merits by the appropriate Regional Water Authority.

In practice, however, for discharges of effluents to surface waters, it has become traditional to use the so-called Royal Commission standards of 1912. These require the suspended solids content of the discharge not to exceed 30 mg/litre and the BOD not to exceed 20 mg/litre, provided that the effluent undergoes an 8-fold dilution in the receiving water, and that the BOD of the latter does not exceed 2 mg/litre.

No discharge is permitted without the consent of the competent Regional Water Authority. Any such consent to discharge effluent into a watercourse may be made subject to the fulfillment of certain conditions; failure to comply with those conditions is punishable by a fine. A consent to discharge effluents into a public sewer may also be made subject to certain conditions; the Authority may, in addition, require the discharger to pay certain costs for the treatment of the effluent.

United States of America

Under the Clean Air Act the US Environmental Protection Agency has promulgated emission standards for kraft pulp mills. These standards are shown in Table 12I.

Table 12I: Performance standards for new kraft pulp mills. (USA)

Source	Pollutant	Emission level	Monitoring requirement
Recovery furnace	Particulate	0.044 gr/dscf (0.10 g/dscm) corrected to 8% oxygen	No requirement
	Opacity	35%	Continuous
	TRS (a) straight recovery	5ppm by volume corrected to 8% oxygen	Continuous
	(b) cross recovery	25ppm by volume corrected to 8% oxygen	
Smelt dissolving tank	Particulate	0.2 lb/ton (0.1 g/kg)	No requirement
	TRS	0.0168 lb/ton (0.0084 g/kg)	No requirement
Lime kiln	Particulate (a) gaseous fuel	0.067 gr/dscf (0.15 g/dscm) corrected to 10% oxygen	No requirement
	(b) liquid fuel	0.13 gr/dscf (0.30 g/dscm) corrected to 10% oxygen	No requirement
	TRS	8ppm by volume corrected to 10% oxygen	Continuous
Digester, brown stack washer, evaporator, oxidation, or stripper systems	TRS	5ppm by volume corrected to 10% oxygen	Continuous
		* exceptions; see standards	Effluent gas incineration temperature; scrubber liquid supply pressure and gas stream pressure loss

(a) constructed after June 11 1973 and before May 19 1978

(b) constructed after May 18 1978

Under the Federal Water Pollution Control Act Amendments of 1972, the US Environmental Protection Agency has issued effluent limitations for the pulp, paper and paperboard point source category. Effluent limitations are given both for existing (Table 12J) and for new (Table 12K) plants. For the former, limitations are given both for the "best practicable control technology currently available" (BPT) and for the "best available technology economically achievable" (BAT).

As well as the limits given in Table 12K, additional limits exist for operations such as wet barking, log washing, or chip washing; the use of log flumes or log ponds etc; for details see the Code of Federal Regulations Title 40, part 430 (reference 19).

Table 12J: Effluent limitations for existing pulp and paper plants (USA)

Process and characteristics	Effluent limitations (a)			
	Max. for any 1 day		Max. ave. of daily values for 30 consec. days	
	BPT	BAT	BPT	BAT
<u>Unbleached kraft</u>				
BOD ₅	5.6	2.7	2.8	1.35
Total suspended solids	12.0	3.7	6.0	1.85
Colour	-	15.0	-	10.0
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0
<u>Sodium based NSSC</u>				
BOD ₅	8.7	4.5	4.35	2.25
Total suspended solids	11.0	5.0	5.5	2.5
Colour	-	75% removal	-	75% removal
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0
<u>Ammonia base NSSC</u>				
BOD ₅	8.0	6.4	4.0	3.2
Total suspended solids	10.0	5.2	5.0	2.6
Colour	-	75% removal	-	75% removal
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0
<u>Unbleached kraft NSSC (cross recovery)</u>				
BOD ₅	8.0	3.2	4.0	1.6
Total suspended solids	12.5	4.2	6.25	2.1
Colour	-	25.0	-	12.5
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0
<u>Paperboard from waste paper</u>				
BOD ₅	3.0	1.5	1.3	0.65
Total suspended solids	5.0	2.5	1.6	0.8
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

Process and characteristics	Effluent limitations		
	Max. for any 1 day (BPT)	Max. ave. of daily values for 30 consec. days (BPT)	Max. annual ave. of daily values for 1 year (BPT)
<u>Dissolving kraft</u>			
BOD ₅	23.6	12.25	6.9
Total suspended solids	37.3	20.05	11.05
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Market bleached kraft</u>			
BOD ₅	15.45	8.05	4.5
Total suspended solids	30.4	16.4	9.0
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>BCT bleached kraft</u>			
BOD ₅	13.65	7.1	4.0
Total suspended solids	24.0	12.9	7.1
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Fine bleached kraft</u>			
BOD ₅	10.6	5.5	3.1
Total suspended solids	22.15	11.9	6.55
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Papergrade sulfite below pit wash</u>			
BOD ₅	31.8	16.55	9.3
Total suspended solids	43.95	23.65	13.0
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Dissolving sulfite pulp</u>			
BOD ₅	41.4	21.5	12.1
Total suspended solids	70.65	38.05	20.9
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Groundwood chemi-mechanical</u>			
BOD ₅	13.5	7.05	3.95
Total suspended solids	19.75	10.65	5.85
pH	5.0-9.0	5.0-9.0	5.0-9.0

Process and characteristics	Effluent limitations		
	Max. for any 1 day (BPT)	Max. ave. of daily values for 30 consec. days (BPT)	Max. annual ave. of daily values for 1 year (BPT)
<u>Groundwood thermo-mechanical</u>			
BOD ₅	10.6	5.55	3.1
Total suspended solids	15.55	8.35	4.6
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Groundwood-CMN papers</u>			
BOD ₅	7.45	3.9	2.2
Total suspended solids	12.75	6.3	3.75
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Groundwood-fine papers</u>			
BOD ₅	6.85	3.6	2.0
Total suspended solids	11.75	6.3	3.45
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Sodab</u>			
BOD ₅	13.7	7.1	4.0
Total suspended solids	24.5	13.2	7.25
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Deink</u>			
BOD ₅	18.1	9.4	5.3
Total suspended solids	24.05	12.95	7.1
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>NI fine papers</u>			
BOD ₅	8.2	4.25	2.4
Total suspended solids	11.0	5.9	3.25
pH	5.0-9.0	5.0-9.0	5.0-9.0

Process and characteristics	Effluent limitations		
	Max. for any 1 day (BPT)	Max. ave. of daily values for 30 consec. days (BPT)	Max. annual ave. of daily values for 1 year (BPT)
<u>NI tissue papers</u>			
BOD ₅	11.4	6.25	3.5
Total suspended solids	10.25	5.0	2.85
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>NI tissue (FWP)</u>			
BOD ₅	13.7	7.1	4.0
Total suspended solids	17.05	9.2	5.05
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Papergrade sulfite (drum wash)</u>			
BOD ₅	26.6	13.9	7.8
Total suspended solids	43.95	23.65	13.0
pH	5.0-9.0	5.0-9.0	5.0-9.0
<u>Papergrade sulfite market pulp</u>			
BOD ₅	40.0	20.85	-
Total suspended solids	49.5	26.65	-
pH	5.0-9.0	5.0-9.0	-

a. Values are expressed in kg/1000 kg of product, except for colour and pH. Colour is measured by the method of the National Council for Air and Stream Improvement (Inc.); colour units are to be assumed equal to mg/litre.

Table 12K: Effluent limitations for new pulp and paper plants (USA)
(in kg/1000 kg of products, except for colour (a) and pH)

Process and characteristics	Max. for any 1 day	Max. ave. of daily values for 30 consec. days
<u>Unbleached kraft</u>		
BOD ₅	3.1	1.55
Total suspended solids	7.5	3.75
Colour	15.0	10.0
pH	6.0-9.0	6.0-9.0
<u>Sodium based NSSC</u>		
BOD ₅	5.2	2.6
Total suspended solids	7.7	3.85
pH	6.0-9.0	6.0-9.0
<u>Ammonia base NSSC</u>		
BOD ₅	7.5	3.75
Total suspended solids	7.5	3.75
pH	6.0-9.0	6.0-9.0
<u>Unbleached kraft NSSC (cross recovery)</u>		
BOD ₅	3.8	1.9
Total suspended solids	8.0	4.0
Colour	25.0	12.5
pH	6.0-9.0	6.0-9.0
<u>Paperboard from waste paper</u>		
BOD ₅	1.5	0.75
Total suspended solids	4.0	2.0
pH	6.0-9.0	6.0-9.0

(a) As measured by the method of the National Council for Air and Stream Improvement (Inc.); colour units are to be assumed equal to mg/litre.

3.12.4. References

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3.13. TANNING

Tanning is the process whereby animal hides and skins are converted into leather.

3.13.1. Outline of process

Hides and skins contain matter which must be removed before tanning, as such, can be carried out. The first stage in the tanning process is therefore hide preparation. After this has been completed, the hides and skins are treated with an appropriate tanning agent. The leather thus produced then undergoes various finishing operations so as to achieve the desired surface finish and mechanical properties.

3.13.2. Sources of pollution

Hide preparation - In what are called the beamhouse processes, hides are prepared for tanning in a number of stages, of which the first is washing and soaking. This removes dirt, blood, manure and non-fibrous proteins, as well as the large amounts of salt usually added as a preservative to enable the hides to be stored for long periods.

The next stage is liming and unhairing, in which the soaked hides are treated with a mixture of lime slurry and a solution of sodium sulfide. This destroys hair, and causes the hides to swell so that they can be more easily penetrated by the tanning agent. If a hair-saving is used, the hair must be removed mechanically. With hair pulping, the hair is completely destroyed.

Liming and unhairing is followed by fleshing, i.e. the removal of any remaining muscle and fatty tissues (as an alternative, fleshing may be carried out directly after washing and soaking).

Finally, the hides are delimed with weak acids and/or acid salts, and bated with a proteolytic enzyme (pancreatin, trypsin), which peptizes the protein fibres and removes unwanted proteins (elastin).

For sheepskins, the beamhouse processes are replaced by a degreasing stage, in which a suitable organic solvent is used. Solvent losses are usually extremely small.

Of the beamhouse processes, washing and soaking, and liming and unhairing both produce substantial amounts of waste waters heavily contaminated with organic matter, though this is reduced if a hair-saving process is used. Beamhouse wastes are combined with tanhouse wastes (see below) before treatment or discharge to sewers.

Tanning - The tanning process used, namely vegetable tanning (by means of plant extracts, such as vegetable tannins), chrome tanning (in which basic chromium sulfate in an acid medium is used), or chrome/vegetable tanning (semi-chrome tanning), will depend on the type of leather to be produced.

When hides and skins are to be chrome or semi-chrome tanned, they must first be pickled (i.e. acidified in sodium chloride solution) to prevent precipitation of chromium salts.

Tanning itself is carried out by suspending the hides for long periods in vats containing a solution of tanning agent.

After chrome tanning, excess tanning liquor is removed by pressing ("samming"); the leather is then retanned under neutral conditions with a chrome, vegetable or synthetic tanning agent. This is followed by colouring, and by fatliquoring to add oils to replace the natural oils lost during the preceding stages.

Tanhouse effluents, together with those from the beamhouse processes, are screened to remove solid matter, such as flesh, hair, etc., and may then be subjected to biological treatment in a percolating filter or activated-sludge plant. As an alternative, they may be discharged into public sewers for treatment together with domestic sewage. Some pretreatment may then be necessary, e.g., flow equalization and mixing to reduce gross variations in flow-rates and composition, sedimentation, neutralization, and removal of chromium salts and sulfides. It may also be possible to reduce effluent discharges by reuse of such solutions as the pickle and chrome tan liquors.

3.13.3. Discharge standards

Brazil

Effluent standards for tanneries for the State of Sao Paulo are given in Table 13A. The standards are based on bibliographical research, consultations with industry and field studies as well as investigations into the best existing treatment systems including their economic feasibility.

Table 13A: Standards for discharges from tanneries in the
State of Sao Paulo, Brazil

		Kg of tanned hide	
		Maximum in any day	Average over 30 consecutive days
Vegetable tannage	BOD	5.4	2.7
	COD	26.2	13.1
	Suspended solids	19.4	9.7
	Trivalent chromium	0.1	-
	Sulfide	0.5	0.24
Chrome and vegetable tannage	BOD	8.8	4.4
	COD	32.4	16.2
	Suspended solids	8.6	4.3
	Trivalent chromium	0.4	0.2
	Sulfide	0.3	0.15

pH values between 6 and 9

France

No legal standards have been laid down for tannery discharges in France. However, tanneries were included among "classified establishments" by the Law of 19 December 1917, and were in particular listed among the second category of such establishments. Their startup therefore requires the authorization of the Prefect, and such authorization may include requirements as to discharges. In addition, the Ministerial Instructions of June 1953 list certain recommendations for discharges from classified establishments. Those relevant to tanneries are shown in Table 13B.

Table 13B: Recommendations for discharges from tanneries into surface waters (France)

Characteristic	Recommended maximum value
pH	5.5 - 8.5
Suspended solids (mg/litre)	30
BOD ₅ (mg/litre)	40
Dissolved oxygen (mg/litre)	5

The surveillance of discharges from tanneries, as classified establishments, is the responsibility of the Inspectors of Classified Establishments. Where the conditions laid down by the Prefect in authorizing the startup of a tannery are not satisfied, he is empowered to specify a period of time within which the necessary changes are to be made. If, on the expiry of this period, the discharges are still unsatisfactory, he can arrange for the necessary work to be carried out at the expense of the owner of the tannery concerned, or may order its closure. In addition, fines may also be imposed under the 1917 Law, under the Water Law of 16 December 1964, or under the Rural Code, as appropriate.

Germany (Federal Republic)

No legal standards have been laid down for tannery discharges in the Federal Republic of Germany, but certain general recommendations concerning industrial discharges have been published. These apply both to discharges into public sewers and into surface waters. The items relevant to tanneries have been extracted from these recommendations, and are shown in Table 13C (standards published by the Abwassertechnische Vereinigung) and Table 13D (standards published by the Länderarbeitsgemeinschaft Wasser).

Table 13C: Recommendations for discharges from tanneries into public sewers (FRG)

Characteristic	Recommended value
pH	6.5 - 9.5
Non-biodegradable material (ml/litre)	1.0
Sulfate (mg/litre)	400
Total chromium (mg/litre)	4
Chromate (mg/litre)	0.5
Solids	Must not block sewers
Odours	Must not be noticeable
Gases (including hydrogen sulfide)	Must not be present in hazardous concentrations

Table 13D: Recommendations for discharges from tanneries into surface waters (FRG)

Characteristic	Type of treatment	Recommended mean value
Settleable solids (ml/litre)	all	0.3
Floating matter	Mechanical	Not to be visible to the naked eye
pH	Chemical	6.0 - 9.0
Potassium permanganate consumption (mg/litre) (a)	Chemical	400
	Biological	150
BOD ₅ (mg/litre) (a)	Chemical	200
	Biological	80
Sulfide (mg/litre)	Chemical	2
Total chromium (mg/litre)	Chemical	2
Hexavalent chromium (mg/litre)	Chemical	0.5
Material extractable by petroleum ether (mg/litre)	Chemical	10

(a) After prior mechanical treatment

India

The tolerance limits for tannery effluents discharged into surface waters are specified in Indian Standard IS:2490, part III, (1974); these are shown in Table 13E.

Table 13E: Tolerance limits for tannery effluents discharged into inland surface waters (India)

Characteristic	Tolerance limit	
	Chrome tanning	Vegetable tanning
Chlorides (as Cl) (mg/litre)	1000	1000
BOD ₅ (mg/litre) new plants	30	30
BOD ₅ (mg/litre) existing plants	30	100
Chromium VI (as Cr) (mg/litre)	0.1	-
Suspended solids (mg/litre)	-	100
pH	5.5 - 9.0	5.5 - 9.0
Colour and odour	-	Absent

Italy

The Law of 10 May 1976 prescribing rules for the protection of waters against pollution contains limiting values for the acceptability of industrial effluents from new plants, depending on whether they are discharged into surface waters or into public sewers. The items relevant to tannery discharges are given in Table 13F.

Characteristic	Limiting values (mg/litre)	
	Surface waters	Public sewers
Chlorides (as Cl)	1000	1000
BOD ₅	30	30
BOD ₅ (existing plants)	30	100
Chromium VI (as Cr)	0.1	-
Suspended solids	-	100
pH	5.5 - 9.0	5.5 - 9.0
Colour and odour	-	Absent

**Table 13F: Limiting values for acceptability of tannery discharges
from new plants (Italy)**

Characteristic	Limiting values for discharges into:	
	Surface waters	Public sewers
pH	5.5 - 9.5	5.5 - 9.5
Colour	Not perceptible(a)	Not perceptible(b)
Odour	Must not cause any inconvenience or nuisance	
Coarse solids (1 cm)	None	None
Total suspended solids (mg/litre)	80	80 - 200
BOD ₅ (mg/litre)	40	40 - 250
COD (mg/litre)	100	100 - 500
Arsenic (as As) (mg/litre)	0.5	0.5
Chromium III (as Cr) (mg/litre)	2	4
Chromium VI (as Cr) (mg/litre)	0.2	0.2
Sulfates (as SO ₄) (mg/litre)	1000	1000
Sulfides (as H ₂ S) (mg/litre)	1	2
Chlorides (as Cl) (mg/litre)	1200	1200
Total ammonia (as NH ₄) (mg/litre)	15	30
Animal and vegetable fats and oils (mg/litre)	20	40
Mineral oils (mg/litre)	5	10
Aromatic organic solvents (mg/litre)	0.2	0.4
Total coliforms (MPN/100 ml)	20,000	20,000
Faecal coliforms (MPN/100 ml)	12,000	12,000

Singapore

The discharge of industrial effluents (generally referred to as trade effluents) into public sewers or water courses is governed by a general set of standards stipulated in the Trade Effluent Regulations 1976. The items relevant to tannery discharges are shown in Table 13G. Controlled watercourses are defined as watercourses from which water supplied by the Public Utilities Board is obtained, but excluding those from which water is pumped into a main belonging to the Board.

Table 13G: Standards for the discharge of tannery effluents (Singapore)

Characteristic	Standards for discharges into:		
	Public sewers	Watercourses	Controlled watercourses
pH	6 - 9	6 - 9	6 - 9
Colour (Lovibond units)	-	7	7
Total suspended solids (mg/litre)	400	50	30
BOD ₅ (mg/litre)	400	50	20
COD (mg/litre)	600	100	60
Arsenic (mg/litre)	5	1	0.05
Chromium III and VI (mg/litre)	5.0	1	0.05
Sulfates (as SO ₄) (mg/litre)	1000	500	200
Chlorides (as chloride ion) (mg/litre)	1000	600	400
Sulfides (as S) (mg/litre)	1	0.2	0.2
Grease and oil (mg/litre)	60	10	5

United Kingdom

No legally enforceable standards exist in the United Kingdom for the discharge of tannery effluents, either to surface waters or to sewers; each case is considered on its merits by the appointed Regional Water Authority.

In practice, the discharge of effluents to surface waters has been governed by the so-called Royal Commission standards of 1912. These require the suspended solids content of the discharge not to exceed 30 mg/litre and the BOD not to exceed 20 mg/litre, provided that the effluent undergoes an 8-fold dilution in the receiving water, and that the BOD of the latter does not exceed 2 mg/litre.

Subject to certain exemptions, no tannery effluent may be discharged into a public sewer without the consent of the appropriate Water Authority; such a consent may be made conditional on the fulfillment of certain requirements and the payment of certain charges. The same system applies to discharges into watercourses; contraventions of the conditions imposed by the Water Authority are punishable by fines.

The Yorkshire Water Authority has produced guidelines for discharge into public sewers and certain items in these guidelines which are relevant to tannery wastes, are shown in Table 13H. Notwithstanding these guidelines, actual levels for any particular tannery will be determined by negotiation with the Authority.

Table 13H: Guidelines for the discharge of tannery wastes into public sewers
 (Yorkshire Water Authority, UK)

Characteristic	Max. indicative value
Suspended solids (mg/litre)	500
pH	5 - 10
Sulfides (mg/litre) (defined as compounds that liberate hydrogen sulphide on acidification)	10
Total chromium (as Cr) (mg/litre)	5
Total non-ferrous metals (mg/litre) (excluding alkali and alkaline earth metals)	30
Total soluble non-ferrous metals (mg/litre) (excluding alkali and alkaline earth metals)	10

United States of America

Under the Federal Water Pollution Control Acts Amendments of 1972, the US Environmental Protection Agency has issued detailed effluent limitations, guidelines and standards for the leather tanning and finishing industry point source category. This is divided into the following subcategories:

hair pulp unhairing with chrome tanning and finishing;
 hair save unhairing with chrome tanning and finishing;
 unhairing with vegetable or alum tanning and finishing;
 finishing of tanned hides;
 vegetable or chrome tanning of unhaired hides;
 unhairing with chrome tanning and no finishing.

Guidelines are given both for existing and for new tanneries, and both for the "best practicable control technology currently available" (BPT) and for the "best available technology economically achievable" (BAT). The limitations apply only to discharges and to the introduction of pollutants into publicly-owned treatment works, and are shown in Table 13I.

Table 13I: Effluent limitations for tanneries (USA) (kg/1000 of raw materials)

HAIR PULP UNHAIRING WITH CHROME TANNING AND FINISHING						
Characteristic	Existing tanneries				New tanneries	
	Max. for any 1 day		Max. ave. of daily values for 30 consec. days		Max. for any 1 day	Max. ave. of daily values for 30 consec. days
	BPT	BAT	BPT	BAT		
BOD ₅	8.0	2.8	4.0	1.40	8.0	4.0
Total suspended solids	10.0	3.0	5.0	1.50	10.0	5.0
Chrome	0.20	0.1	0.10	0.05	0.10	0.05
Oil and grease	1.50	1.00	0.75	0.53	1.00	0.53
Sulfide	-	0.01	-	0.005	-	-
TKN	-	0.54	-	0.27	-	-
Faecal coliforms (max. at any time)	-	400 counts /100 ml	-	400 counts /100 ml	-	-
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

HAIR SAVE UNHAIRING WITH CHROME TANNING AND FINISHING

BOD ₅	9.2	3.2	4.6	1.60	9.2	4.6
Total suspended solids	11.6	3.0	5.0	1.80	11.6	5.8
Chrome	0.24	0.12	0.12	0.06	0.24	0.12
Oil and grease	1.80	1.26	0.90	0.63	1.80	0.90
Sulfide	-	0.012	-	0.006	-	-
TKN	-	0.64	-	0.32	-	-
Faecal coliforms (max. at any time)	-	400 counts /100 ml	-	400 counts /100 ml	-	-
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

UNHAIRING WITH VEGETABLE OR ALUM TANNING AND FINISHING

Characteristic	Existing tanneries				New tanneries	
	Max. for any 1 day		Max. ave. of daily values for 30 consec. days		Max. for any 1 day	Max. ave. of daily values for 30 consec. days
	BPT	BAT	BPT	BAT		
BOD ₅	7.6	2.6	3.8	1.30	7.6	3.8
Total suspended solids	9.6	2.8	4.8	1.40	9.6	4.8
Chrome	0.1	0.1	0.05	0.05	0.01	0.05
Oil and grease	1.50	1.0	0.75	0.50	1.50	0.75
Sulfide	-	0.01	-	0.005	-	-
TKN	-	0.01	-	0.005	-	-
Faecal coliforms (max. at any time)	-	400 counts /100 ml	-	400 counts /100 ml	-	-
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

FINISHING OF TANNED HIDES

BOD ₅	3.2	1.0	1.6	0.50	3.2	1.6
Total suspended solids	4.0	1.2	2.0	0.60	4.0	2.0
Chrome	0.20	0.04	0.10	0.02	0.02	0.10
Oil and grease	0.50	0.48	0.25	0.24	0.50	0.25
Sulfide	-	0.004	-	0.002	-	-
TKN	-	0.2	-	0.10	-	-
Faecal coliforms (max. at any time)	-	400 counts /100 ml	-	400 counts /100 ml	-	-
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

VEGETABLE OR CHROME TANNING OF UNHAIRD HIDES

Characteristic	Existing tanneries				New tanneries	
	Max. for any 1 day		Max. ave. of daily values for 30 consec. days		Max. for any 1 day	Max. ave. of daily values for 30 consec. days
	BPT	BAT	BPT	BAT		
BOD ₅	9.6	3.2	4.8	1.60	9.6	4.8
Total suspended solids	12.0	3.6	6.0	1.80	12.0	6.0
Chrome	0.12	0.12	0.06	0.06	0.12	0.06
Oil and grease	1.80	1.26	0.90	0.63	1.80	0.90
Sulfide	-	0.012	-	0.006	-	-
TKN	-	0.62	-	0.31	-	-
Faecal coliforms (max. at any time)	-	400 counts /100 ml	-	400 counts /100 ml	-	-
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

UNHAIRING WITH CHROME TANNING AND NO FINISHING

BOD ₅	5.6	1.4	2.8	0.70	5.6	2.8
Total suspended solids	6.8	1.6	3.4	0.80	6.8	3.4
Chrome	0.20	0.06	0.10	0.03	0.20	0.10
Oil and grease	0.70	0.68	0.35	0.34	0.70	0.35
Sulfide	-	0.006	-	0.003	-	-
TKN	-	0.28	-	0.14	-	-
Faecal coliforms (max. at any time)	-	400 counts /100 ml	-	400 counts /100 ml	-	-
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

3.13.4. References

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